

# THE DEVELOPMENT OF TRANSITION METAL CHEMISTRY IN THE UNITED STATES OF AMERICA

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## ABSTRACT

The study of complex inorganic compounds in America began more than a century ago, but very few chemists were involved in it until the 1920s. Since that time, research on both the theoretical and descriptive aspects of the subject has expanded at a tremendous rate. The early work was concerned largely with the metal amines and hydrates, but in more recent years, it has expanded into phosphines, arsines, carbonyls, complexes of elemental oxygen and nitrogen, compounds containing metal-metal bonds, and a variety of organometallics. The development of modern instrumentation has been of great help, especially in the study of bonding and structure.

New oxidation states and new coordination numbers have been found, and the stereochemistry of the latter have been explored. Reaction mechanisms have been studied extensively. There is now a great deal of activity in the use of coordination compounds as catalysts and in their role in biochemistry.

Although Americans are proud of their accomplishments in the field of coordination chemistry, they recognize that chemists in many parts of the world have contributed and that no country can stand alone in the development of this or any other science.

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Chemists in the United States have done a great deal of work on coordination compounds and have compiled an enviable record. However, many other countries likewise have contributed in important ways—consider, for example, the fine work that has gone on in England, Denmark, Australia, Japan, Switzerland and Italy, to name only a few. We must be careful to avoid developing a spirit of national rivalry in research, for we are not contestants, but collaborators. Often, a discovery made by chemists in one country is carried forward by those in another—to the credit of both countries. Indeed, we might not be able to report at all if the initial steps had not been taken in Switzerland almost eighty years ago.

The task of condensing into a short paper the most significant developments in coordination chemistry in the United States is an almost impossible one.

There are at least a hundred groups of scientists now doing research on the chemistry of coordination compounds in the United States. Many other groups have made significant contributions, but are no longer active. I have selected a few items that seem to me to be particularly significant, but I recognize that another author might well have selected quite a different list. There is much other work that I should like to include, but must omit for lack of space. Arbitrarily, I have omitted hydrogen bonding, although it is of great importance, and have given scant attention to the main group elements, for, while their coordination compounds are of interest and

significance, they are labile and their chemistry is of less interest (at least, to me) than that of the transition metals.

It has been known for a long time that even the alkali metal ions form complexes, but the bonding in these is quite different from that in complexes of the transition metals, for there is not, and cannot be, any back bonding. There might even be some question as to whether they can be referred to as coordination compounds. However, the remarkable complexes formed between cyclic polyethers and salts of the alkali and alkaline earth ions (as well as heavier metal ions) must be mentioned here, for they have the remarkable property of being soluble in non-polar solvents<sup>1</sup>. This opens areas for study of catalysis, transport across membranes and hydrolysis of esters. Such applications have already been studied by several investigators.

The size of the polyether ring determines, in large measure, what cations can be fitted into the complex. Those with four oxygen atoms in the ring show selectivity for lithium ions, those with five oxygens for sodium, and those with six oxygens, for potassium. Many polyethers have been synthesized and found to coordinate a variety of cations. Even the ammonium ion forms a complex, which shows that the bonding is purely electrostatic. The structures of the barium complex<sup>2</sup> and of several transition metal complexes have been studied. The cobalt(II) compounds evidently form dimeric or polymeric units<sup>3</sup>.

Similarly, the treatment of the poly-acids and their salts has been given only scant treatment. These interesting substances have not been studied widely in America, perhaps because such study is most difficult. On the basis of radius ratios and interionic forces, Pauling suggested structures for them<sup>4</sup>. Keggin's x-ray study of the complexes showed this suggestion to be inaccurate, but based on correct principles<sup>5</sup>. Later work, largely by L. C. W. Baker and his students, has done a great deal to clarify the structures of the heteropoly acids and to show that the Miolati-Rosenheim coordination theory of structure is untenable. New types of polyacids have also been synthesized and it has been shown that some heteropoly acids contain non-titratable hydrogen<sup>6</sup>. The long list of papers on polyacids can be traced from the most recent one<sup>7</sup>.

Work on 'complex inorganic compounds' began early in the United States—long before Alfred Werner was even born. Genth and Gibbs did a good deal of work in the 1850s on what they called the 'new addition compounds', and they published a book on the subject in 1856<sup>8</sup>. Genth was apparently the first person to clearly recognize the distinction between chloropentammine cobalt(III) salts and the aquopentammines<sup>9</sup>. It should be mentioned, in passing, that the first optical resolution of a complex inorganic compound was carried out by one of Werner's American students, V. L. King<sup>10</sup>.

In spite of this early beginning, little work on coordination compounds was done in America until the 1920s and the early 1930s. At that time, Blanchard was active in the study of the formation and structure of metal carbonyls<sup>11</sup>, Thomas was studying solated complexes<sup>12</sup>, Latimer, through his book on oxidation-reduction potentials<sup>13</sup>, called attention to the phenomenon of valence stabilization through coordination (although he did not use that term) and Lamb did important work on the conductivities and the acid-base character of metal amines<sup>14</sup>. Lewis published his famous theory

of acids and bases in the early 1920s<sup>15</sup>. In this, he considered an acid to be the acceptor atom of a complex and a base to be the donor atom, the degree of covalent binding being measured by the strength of the acid.

Pauling published his first research paper in 1923. His contributions have been tremendous—one might mention among the greatest of them his development of the valence bond theory, the 'magnetic criterion' for 'ionic' and 'covalent' complexes, the theory of back bonding, and his development of the theory of resonance. Soon after Pauling entered the field, and partly because of his work, the field began to expand rapidly. In more recent years, this expansion has been greatly aided, of course, by the development of instruments for the measurement of infra-red, nuclear magnetic resonance, and mass spectra, of powerful new instrumentation and computer methods for the determination of structures by x-ray analysis, of Mössbauer spectroscopy and of new methods such as polarography and column chromatography.

Although it is customary to think that complexes are formed by the union of metal ions or metal atoms with anions or non-metallic molecules, these are not completely accurate concepts. Parry<sup>16</sup> has shown that the amine adducts of boron hydrides can properly be considered to be coordination compounds of boron, in which the hydride ions in  $[\text{BH}_4]^-$  are replaced successively by amine molecules. This leads to the series  $[\text{BH}_4]^-$ ,  $[\text{BH}_3\text{NR}_3]$ ,  $[\text{BH}_2(\text{NR}_3)_2]^+$ ,  $[\text{B}(\text{NR}_3)_3]^{2+}$  and  $[\text{B}(\text{NR}_3)_4]^{3+}$ , the last of which has not yet been prepared. It is a significant concept in that it brings the metalloids into line with the metals.

On the other side of the picture, it has been shown that ligands may carry a positive charge—that is, they may be cations. For example, the  $\beta$ -aminoethyltrimethylammonium ion,  $[\text{NH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_3]^+$  can coordinate with positively charged metallic ions. Using this ligand, complex cations

with an ionic charge of  $+8$   $[\overset{\text{II}}{\text{ML}}_6]^{8+}$  have been synthesized<sup>17</sup>.

The significance of coordination chemistry in understanding reactions that occur in the general area of non-aqueous solvents has been elucidated in the formulation of the coordination model by Drago and his students<sup>18</sup>. Organic and many inorganic solvents were treated by a unified model which emphasized the ligand donor strength and solvating ability of the solvent as opposed to solvent self-ionization.

When Pauling's valence bond theory proved to be inadequate in some respects, it was translated into ligand field theory and then into molecular orbital theory by several American investigators<sup>19-22</sup>. The electronic energy levels were assigned in many complexes, and a good deal of definite information was obtained on the sources of spectral intensities of electronic bands.

## UNUSUAL OXIDATION STATES

In these days, metals can be stabilized in a wide variety of oxidation states and we are no longer surprised to read of cobalt(I), chromium(IV), or even vanadium(-I). These developments, however, have come only in the last decade or so. Americans have contributed their share. For example, Gray<sup>23</sup> has isolated soluble compounds of the elusive gold(II) which had been

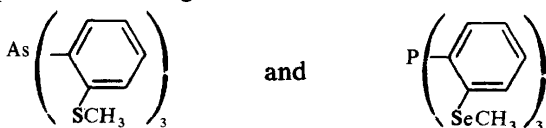
unsuccessfully sought for many years. Soluble compounds of berkelium(IV)<sup>24</sup>, californium(IV)<sup>25</sup>, neptunium(V)<sup>26</sup>, uranium(V)<sup>27</sup>, and nickel(IV)<sup>28</sup> have been synthesized. Compounds in some of these oxidation states have also been prepared by others, using quite different methods<sup>29</sup>, so the results are doubly confirmed.

In a most interesting series of researches, Drickamer and his students have observed that both high spin and low spin iron(III) complexes in the solid state, when subjected to pressures in the 100 kilobar range, are reduced to the iron(II) state. This process is reversible<sup>30</sup>.

## COORDINATION NUMBER

Until recent years, the coordination numbers four and six were the only ones that received much attention, but now several others have been shown to be easily achieved. The metal in a complex, even though it is coordinately saturated in the usual sense, can sometimes add another donor atom, thus increasing its coordination number. This may lead to an unusual or unexpected coordination number. Thus, the square planar molecule  $[\text{IrCl}(\text{CO})(\text{PR}_3)_2]$  readily adds a molecule of sulphur dioxide<sup>31</sup>, giving a compound in which the coordination number of the metal is five. In some cases, the metal may also lose electrons to the newly added group, and thus increase its own oxidation number as well as its coordination number. For example, the iridium(I) complex shown above adds a mole of hydrogen to give the iridium(III) compound  $[\text{IrH}_2\text{Cl}(\text{CO})(\text{PR}_3)_2]$ <sup>32</sup>. Oxidative addition is very important in catalysis, for if a complex is to have catalytic properties, it must have an open site in the coordination sphere where a reacting molecule can attach itself<sup>33</sup>. Oxidative addition reactions have had recognized importance in inorganic biochemistry for many years (e.g. in the action of haemoglobin), but their application to industrial processes has been fully recognized only recently.

Five coordinate complexes were almost unknown a decade ago, but now scores, if not hundreds, of such substances are known and well characterized. Certainly, this is not exclusively or even primarily a field in which Americans have worked, but several Americans have contributed significantly to our knowledge of five coordinate complexes. For example, the ions  $[\text{Ni}(\text{CN})_5]^{3-}$ ,  $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$  and  $[\text{NiI}_2(\text{HP}(\text{C}_6\text{H}_5)_2)_3]$ <sup>34</sup> have recently been isolated. Some interesting quadricovalent ligands, such as



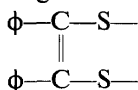
have been shown to give complexes that readily add a fifth group<sup>35</sup>.

Several five coordinate complexes in which the central atom is a non-metal have been studied, also, both as intermediates in reactions and from a theoretical point of view<sup>36</sup>.

Even the coordination number six, which we thought was understood thoroughly, has given us some great surprises. One of the most exciting of the stereochemical discoveries is that some six-coordinate complexes are trigonal

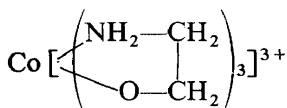
prismatic rather than octahedral. These compounds fall into several groups:

1. Those which contain three rigid bidentate ligands such as



Ligands of this type were prepared only recently and were found to have quite unusual properties<sup>37</sup>. A number of complexes have been prepared, using a variety of ligands and metal ions such as rhenium, tungsten, vanadium and molybdenum. In some cases, the six sulphur atoms have been shown to form an almost perfect trigonal prism about the metal<sup>38, 39</sup>.

2. Those in which a metal ion attaches itself to three atoms in each of two octahedral complexes. For example, two facial-*tris*-(aminoethoxido)cobalt (III) ions



can attach themselves, through their oxygen atoms, to a divalent transition metal ion. This new complex is an almost perfect trigonal prism (Figure 1)<sup>40</sup>.

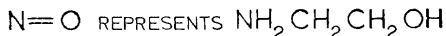
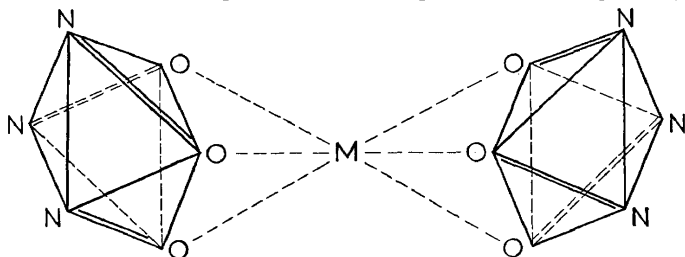


Figure 1. A trimeric complex of aminoethanol in which the terminal metal atoms are at the centres of octahedra and the middle one, at the centre of a trigonal prism

3. Those in which two opposite faces of a *bis*-tridentate chelate are 'capped' by groups that distort the normal octahedral form into a trigonal prismatic form. For example, *tris*-dimethylglyoximato cobalt(III) can be converted to a doubly capped clathro chelate, which assumes a trigonal prismatic form (Figure 2)<sup>41, 42</sup>. Variants of this type are also known<sup>43</sup>.

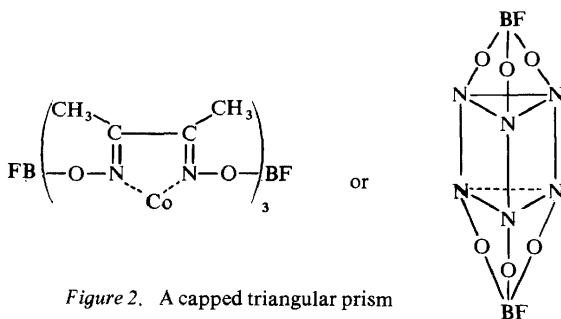


Figure 2. A capped triangular prism

4. Those in which all six coordination sites are occupied by donor atoms which are part of a single rigid ligand molecule. An example of such a ligand is *cis,cis*-1,3,5-*tris*(pyridine-2-carboxaldimino)cyclohexane (Figure 3). The

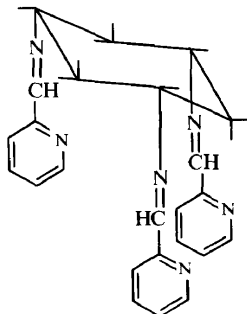


Figure 3. A rigid hexadentate ligand, *cis,cis*-1,3,5-*tris*(pyridine-2-carboxaldimino)cyclohexane

$Zn^{2+}$ ,  $Co^{2+}$ , and  $Mn^{2+}$  complexes have a trigonal prismatic geometry, but the  $Ni^{2+}$  and  $Fe^{2+}$  compounds seem to be octahedral, or nearly so<sup>44</sup>. The ligand made by condensing 1,1,1-*tris*(aminomethyl)ethane with pyridine-2-carboxaldehyde gives a zinc complex which is approximately half way between a regular trigonal prism and a regular octahedron. The  $Ni^{2+}$ ,  $Co^{2+}$  and  $Mn^{2+}$  complexes apparently have similar structures<sup>45</sup>.

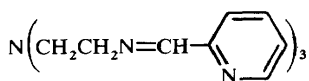
Octahedral complexes of several non-transition metals have been resolved into their optical antipodes, perhaps the most interesting being those of silicon<sup>46</sup>, aluminium<sup>47</sup> and germanium<sup>48</sup>. Although the complexes of the lanthanides have usually been considered to be very weak, some of them have also been found to be inert enough to allow resolution<sup>49</sup>.

The separations in some of these cases were achieved by the classical method of recrystallizing diastereoisomers, but several new and valuable techniques for resolution have also been used. The most widely applied of these depends upon preferential adsorption on asymmetrical crystals, a method which has been studied by Kirschner<sup>50</sup>. Sievers and Mosher have even resolved *tris*-hexafluoroacetylacetonato chromium(III) in the gaseous state in this way<sup>51</sup>.

The study of optically active compounds and of the conformations of complexes has been greatly aided in recent years by an increasing knowledge of circular dichroism, and availability of instruments for its exact measurement. This is certainly not a field in which only Americans have worked, but it is one to which Americans have contributed a good deal<sup>52</sup>.

The achievement of coordination numbers higher than six depends upon proper selection of the metal ion and the ligand<sup>53</sup>. Small, unidentate, highly electronegative anionic donor atoms such as fluoride tend to bring out high coordination numbers. Thus, the coordination number seven is illustrated by  $TaF_7^{2-}$ <sup>54</sup>,  $NbF_7^{2-}$ <sup>54</sup>, and  $ZrF_7^{3-}$ <sup>55</sup>, the structures of which have been determined. Seven coordinate complexes containing resonating oxygen chelates are also well established<sup>53, 56-59</sup> as well as those containing EDTA

and its homologues<sup>60</sup>. A particularly interesting ligand which gives a seven coordinate nickel(II) complex<sup>61</sup> is



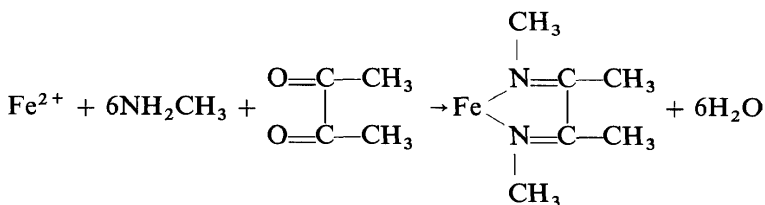
The stereochemistry of eight-coordination shows more variety than that of lower coordination numbers<sup>62</sup>. Hoard and Silverton have analysed the factors that determine the stereochemistry of coordination number eight<sup>63</sup>, complexes being known in quasi cubic<sup>64</sup>, antiprismatic<sup>65</sup>, dodecahedral<sup>66</sup> and approximately hexagonal bipyramidal<sup>67</sup> forms.

Coordination numbers nine<sup>68-71</sup> and ten<sup>69,70</sup> are also well established, and the structures of some of them have been determined.

Returning to the octahedral complexes, the subject of ligand-ligand interactions has received a good deal of attention, especially in regard to stereospecificity. Stereospecific reactions of octahedral complexes containing optically active ligands have been known for a long time, but it was only in 1959 that they were satisfactorily explained<sup>72</sup>. It was pointed out that many five membered chelate rings are puckered and that ring substituents always tend to occupy equatorial positions. Interactions between such rings then exert stereospecific influences on incoming groups.

There are, of course, many other effects of stereochemical interactions between ligands—for example, the metal-donor bond strength. This has been reported by many chemists who have measured stability constants, both in America and elsewhere. The difference in stability between the racemic and meso-forms of the copper(II) and nickel(II) complexes of 2,3-butylenediamine and meso-stilbenediamine furnishes a particularly striking example<sup>73</sup>. Stability constants have also been used in the study of biological materials<sup>74</sup>, of olated complexes<sup>75</sup>, and in many other ways.

Another aspect of ligand interactions has been exploited in reactions which Busch has labeled 'template' reactions<sup>76</sup>, and which have been used to synthesize cyclic organic compounds<sup>77,78</sup> as well as some interesting non-cyclic ones. The principle is that two or more organic molecules are held in fixed positions by coordination to a metal ion, and while held in this way, they react with each other or with other molecules to yield a product which would not otherwise be obtained. For example, in the presence of iron(II) ions, diacetyl and methyl amine react to give a monomeric Schiff's base



while in the absence of the metallic ion, highly polymeric substances are formed<sup>79</sup>.

## RELATIONSHIP BETWEEN STRUCTURE AND REACTIVITY

It is common knowledge that some complexes are inert toward substitution and others are quite labile. Taube<sup>80</sup> has pointed out that complexes in which the metal ion in the complex contains an empty inner orbital tend to be labile, while those that are filled or half filled tend to be inert. The correlation is not perfect, but it is very striking, and has been found to be most useful.

Pearson<sup>81</sup> has recently added to our understanding of the stability of complexes by his popularization of the concept of 'hard' and 'soft' acids and bases. Hard donor ions (e.g.  $F^-$ ,  $OH^-$ ,  $H^-$ ) tend to form stable complexes with hard metal ions (e.g.  $Be^{2+}$ ,  $Al^{3+}$ ) while soft bases (e.g.  $R_2S$ ,  $I^-$ ) tend to combine with soft metal ions (e.g.  $Pt^{2+}$ ,  $Cu^{2+}$ ).

If a ligand contains both a hard donor atom and a soft donor atom, it may coordinate through either, depending upon the nature of the metal ion to which it attaches itself. Thus, the thiocyanate ion coordinates to cobalt (III) through the nitrogen atom, but to mercury(II) through the sulphur atom. It has long been known that the  $:\ddot{O}:\ddot{N}:\ddot{O}:^-$  group, in cobalt(III) compounds, can attach itself through either an oxygen or the nitrogen atom. It is now known that the 'hardness' or 'softness' of a metal ion is modified by the groups which are coordinated to it, and that by suitable modification, ambidentate ligands can be made to attach themselves through either their 'hard' or their 'soft' donor atoms. The study of this phenomenon was begun in Basolo's laboratory and has been continued in a long series of papers by Burmeister<sup>82</sup>, and by others<sup>83</sup>.

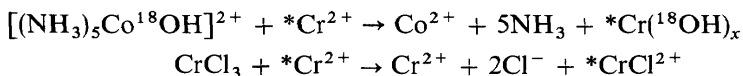
A related type of isomerism concerns bidentate ligands which attach themselves to two unlike metal ions. This is illustrated by the highly polymeric heavy metal cyanides such as  $KFe^{II}Cr^{III}(CN)_6$ , in which the carbon atom can be coordinated either to the iron or to the chromium, and the nitrogen atom to the other. The two isomers are not of equal stability, and on long standing or heating, the  $CrCNFe$  linkage changes to  $CrNCFe$ <sup>83a</sup>.

The stability of complexes toward thermal decomposition was studied by several investigators some years ago<sup>84</sup>, but was then neglected as other aspects of coordination chemistry became more popular. It is now receiving attention in America again. Since it sometimes offers a good synthetic route and is often accompanied by isomerizations, there are some important aspects to be considered<sup>85-88</sup>. A few mass spectrographic studies have also been carried out<sup>89</sup>.

## RATES AND MECHANISMS OF REACTIONS

The subject of reaction mechanisms has received a great deal of attention, both in America and elsewhere. This study depends, first of all, upon a knowledge of the kinetics of reactions. Connick<sup>90</sup>, at the University of California, was a pioneer in this field with his studies of the rates of water exchange of many metallic ions. Taube has contributed to this field, too, by rate measurements in which he used isotopically labeled atoms. His observation that the exchange between  $[Cr(H_2^{18}O)_6]^{3+}$  and  $H_2^{16}O$  has a half life of about forty hours at room temperature is a particularly striking example<sup>91</sup>.

The course of many oxidation-reduction reactions has been followed by the use of labeled atoms<sup>92</sup>, the following being typical



It is clear that there is a bridged intermediate in each of these reactions. When oxyanions such as  $\text{UO}_2^{2+}$  are reduced, one oxygen atom is transferred to the reductant, again showing that a bridged intermediate was formed<sup>93</sup>. The rate and mechanism of oxygen exchange in other oxy-complexes has also been studied<sup>94</sup>. A variety of systems such as Co(III)—Fe(II), Cr(III)—Cr(II) and Co(III)—Cr(II) featuring azide and formate bridges have been shown to utilize two bridges in the transition state for electron transfer<sup>95</sup>.

Many redox reactions, of course, do not proceed through the agency of a bridged intermediate, but by direct electron exchange. The transfer of electrons between ions that differ only in the number of electrons, such as  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{o-phen})_3]^{2+}$  and  $[\text{Fe}(\text{o-phen})_3]^{3+}$ <sup>92</sup> and  $\text{MnO}_4^-$  and  $\text{MnO}_4^-$ <sup>96</sup> have been studied in detail, using isotopic labeling. In the latter case, it was shown that the reaction is first order with respect to both reactants and that there is no interpenetration of the coordination spheres.

A field of inorganic chemistry which has aroused considerable interest has involved rates of electron transfer reactions of coordination complexes, as well as of other reactants in solution. In these reactions, as was pointed out by Libby, the electron transfer can occur in such a short time interval that the molecules in the coordination sheath and in the solvent do not have time to move. Marcus<sup>97</sup> noted that the necessary readjustments of the molecular orientations and positions of ligands and of solvents occur partly before and partly after electron transfer. In the activated complex of the reaction these orientations and positions have adopted some compromise between initial and final properties.

Marcus attacked this problem in 1956, showed that conventional electrostatics could not be used, and developed electrostatics appropriate to this new situation. In 1960, he included the contributions of both the inner coordination shell and the outer solvent sheaths. Equations were thereby derived for the rate constant and for its relation to the rate constants of isotopic exchange electron transfer reactions. In this way, factors influencing the reaction rates have been delineated to include intrinsic effects, such as overall changes in bond length and the thermodynamic driving force. Relations were deduced between electron transfer rates in solution and those at electrodes and further stimulated interaction between researchers in those two fields. Related methods were also used in treating electron transfer reactions of solvated electrons with coordination complexes and in treating chemiluminescence of highly exothermic electric transfer reactions.

Pioneering work on the kinetics and mechanisms of substitution reactions was done by Basolo, Pearson and their students in the early 1950s<sup>98</sup>. Their data are in accord with the concept that reactions of six-coordinate systems take place primarily by a dissociative ( $S_N1$ ) process, and reactions of four-coordinated square planar complexes by an associative ( $S_N2$ ) process. Similar studies were made a little later on substitution reactions of metal carbonyls and organometallic compounds<sup>98,99</sup>.

Wilmarth has been active in this field, too, studying especially *trans-*

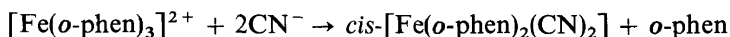
effects in octahedral cobalt(III) complexes. He has observed that in such cases, *trans*-activation is a necessary but not sufficient condition for the existence of a limiting  $S_N1$  substitution mechanism<sup>100</sup>. D. S. Martin has also contributed greatly to the study of the mechanism of substitution reactions, specializing particularly in planar complexes of platinum. In the study of the trichloroammine platinate(II) ion, it was shown that the chloride *trans* to a chloride undergoes solvation ten times as fast as the chloride *trans* to an ammonia molecule. However, the *trans* [Pt(NH<sub>3</sub>)(H<sub>2</sub>O)Cl<sub>2</sub>] isomer, which forms more slowly, is more stable than the *cis* isomer, and eventually becomes the predominant species. Systemization of rate constants in this series has shown that some kinetic effects which have traditionally been attributed to the *trans*-effect are in truth more influenced by the nature of the *cis*-ligand. Additional systems which have been studied involve the anion of Zeise's salt, trichloroethylene-platinate(II), and a number of complexes containing phosphine ligands. It has also been shown that the exchange rate laws for the bromo-complexes are much more complicated than for the corresponding chloro-systems<sup>101</sup>.

The study of multidentate ligand kinetics has been made in some detail. This involves questions of the stepwise nature of the substitution process with flexible multidentate ligands, the mode of transfer of a multidentate ligand from one metal ion to another, and the transfer of metal ions between multidentate ligands<sup>102</sup>.

Some of the photochemical aspects of coordination chemistry have been reviewed recently<sup>103</sup>. The study of the photochemistry of complexes is shedding a great deal of light on their electronic structures.

An interesting substitution reaction involving the inversion of configuration in the reaction of an optically active complex was observed by Bailar and Auten in 1934<sup>104</sup>.

$\Delta$ -*cis*-[Coen<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> + CO<sub>3</sub><sup>2-</sup> → either  $\Delta$ - or  $\Lambda$ - [Coen<sub>2</sub>CO<sub>3</sub>]<sup>+</sup> + 2Cl<sup>-</sup>  
 Comparable complexes of chromium(III) and iridium(III) do not show the inversion. The reaction resembles the famous Walden inversion of organic chemistry, but it follows an entirely different mechanism. Archer<sup>105</sup> has recently found an example of a similar inversion in the reaction



Closely connected with this is the question of how rearrangements of octahedral complexes take place. Werner postulated a bond breaking mechanism to account for the racemization of *tris*-oxalato chromate(III) but, by the use of isotopically labeled oxalate, Long showed that this is incorrect<sup>106</sup>. The alternative to a dissociation mechanism is a twist mechanism, and it is now generally agreed that both bond-breaking and twist mechanisms are involved in *cis-trans* isomerizations and in racemizations. Several types of twist mechanisms can be imagined. Following the first description of a twist mechanism by Ray and Dutt, several Americans have studied the problem<sup>107</sup>. That *tris*-diketonate complexes racemize through a dissociation mechanism is indicated by the fact that mixed complexes [M(dik)<sub>2</sub>(dik')]<sup>n+</sup> are readily formed by the gentle warming of solutions of the two simple complexes, [M(dik)<sub>3</sub>]<sup>n+</sup> and [M(dik')<sub>3</sub>]<sup>n+</sup> and in other ways<sup>108</sup>. However, even with

the *tris*-diketonates, some racemization takes place through a twist mechanism<sup>109</sup>. The racemization of the *tris*-ethylenediamine cobalt(III) ion has been shown to proceed with exchange with labeled ethylenediamine<sup>110</sup>, but that the *tris*-ethylenediamine platinum(IV) ion, without exchange<sup>111</sup>. Presumably, the latter proceeds by a twist mechanism. Complexes which contain ligands that tend to assume a trigonal prismatic configuration would also be expected to racemize by a twist mechanism. The racemization of the *tris*-dipyridyl iron(II) and *tris*-orthophenanthroline iron(II) complexes follows both a twist and a dissociation mechanism<sup>112</sup>.

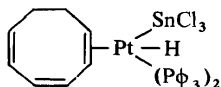
## METAL-ORGANIC COMPOUNDS

The study of organometallic coordination compounds has been pursued in many countries, and it is difficult here, as with other topics, to isolate American work from that done abroad. We can divide the transition metal organic compounds into four main classes:

1. The olefin complexes, the first of which was discovered by Zeise in Germany in 1829.
2. The metal carbonyls, the first of which was observed by Mond in England in 1890.
3. The  $\pi$ -aromatic (ferrocene-like) complexes, discovered by Kealy and Pauson in America in 1951<sup>113</sup>.
4. The  $\pi$ -allylic and related systems.

The four groups overlap somewhat, but this classification will suffice for our purposes.

The early American studies of olefin complexes were made chiefly by organic chemists<sup>114</sup>. However, as the metal-olefin complexes came to be recognized as coordination compounds, the emphasis on their study shifted toward inorganic chemistry. There have been many studies of the nature of the olefin-metal bond, but in recent years, the chief emphasis on these substances has been in connection with industrial processes, such as polymerization and the selective hydrogenation of **olefinic** substances. The isolation of several intermediates in the hydrogenation process has shown that the olefin forms a complex with the metal, expanding the coordination sphere of the latter. A typical example<sup>115</sup> is

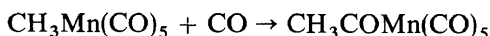


The interesting trichlorostannato group was first recognized as a weakly  $\sigma$ -donating, strongly  $\pi$ -accepting, ligand by Lindsey and his co-workers<sup>116</sup>.

The metal carbonyls have received a great deal of attention in all parts of the world. The classic work of Hieber, in Germany, has borne fruit in studies of synthesis, bonding, reaction kinetics, and catalysis. Americans cannot claim to have made any greater advances in this area than have the chemists of many other countries, but several Americans, even from the earliest times,

have made notable contributions to the theory of bonding in the metal carbonyls<sup>11, 117</sup>, and the structures are now well understood. It is known that in polynuclear carbonyls there are some carbon monoxide molecules bound to a single metal atom and some that are 'ketonic' in nature, binding two metal atoms together. In addition, of course, there may be direct metal-metal bonding [e.g.  $\text{Fe}_2(\text{CO})_9$ ]. In some dinuclear carbonyls, the metals are held together only through metal-metal bonds [e.g.  $\text{Mn}_2(\text{CO})_{10}$ ]. In more recent times, several Americans have made important contributions. Jones and his co-workers<sup>118</sup> have made detailed studies of the bonding in metal carbonyls through the measurement of infra-red spectra and the calculation of force constants, using isotopically labeled carbon and oxygen.

On the more synthetic side, Sternberg, Markby and Wender's synthesis of duroquinone<sup>77</sup> from iron carbonyl and dimethyl acetylene is worthy of note, for it opened new areas of synthetic organic chemistry. Equally important, perhaps, is the study of 'insertion reactions'<sup>119</sup> such as



It has been shown that the carbonyl group in the acetyl moiety is not the one from the added carbon monoxide, and it is inferred that the methyl group migrates from the manganese atom to a carbon atom<sup>120</sup>.

Vaska has exploited the chemistry of the iridium(III) complex  $[\text{IrCl}(\text{CO})(\text{P}\phi_3)_2]$ <sup>121</sup> and the oxidative addition reactions (some of them readily reversible) which it undergoes, and has shown that these compounds have potentially great value as catalysts.

The nitrosyls and carbonyls are often compared, and mixed metal nitrosyl-carbonyls are well known. However, pure nitrosyls corresponding to the volatile metal carbonyls are rare, if not unknown. Complex ions containing the NO group are well known, but their structures and properties are not fully explored, by any means. A study of these substances which Feltham began in England is being continued in America<sup>122</sup>.

A great deal of synthetic work has been done in the field of carbonyl chemistry; unfortunately, only a few examples can be mentioned here. It has long been known that the CO molecules in metal carbonyls can be replaced by other ligands<sup>123</sup>, but the observation that they can react without displacement is recent<sup>124</sup>. Polymeric carbonyls and substituted monomeric ones readily react with the alkali metals to give compounds such as  $\text{NaCo}(\text{CO})_4$  and  $\text{Na}_2\text{Fe}(\text{CO})_4$  and halogen containing carbonyls react with metallic magnesium to give Grignard reagents. Both the alkali metal derivatives and the Grignard reagents can be utilized in the synthesis of organometallic compounds. Carbonyl anions react directly with alkyl iodides to yield organometallic compounds. All of these reactions and many more are discussed by R. B. King, who, with his collaborators, has discovered and exploited several of them<sup>125</sup>.

Another group of organometallic compounds containing delocalized bonds contains the  $\pi$ -allyl complexes and some related materials. In these, the organic radical donates electrons in a  $\sigma$ -type bond and accepts electrons from the metal in a  $\pi^*$ -type bond. The nature of this bond has been studied extensively, chiefly by n.m.r. spectra, by many American workers as well as those abroad. The  $\pi$ -allylic compounds are synthesized by treatment of

metal carbonyls or carbonyl hydrides with olefins<sup>126</sup> or a bromo-olefin<sup>127</sup>. The nickel compound  $[\text{Ni}(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_7)]$  has been made by the reduction of decyclopentadienyl nickel with sodium amalgam. The reduced ring is bonded to the nickel through a  $\pi$ -allyl bond<sup>128</sup>. Since the allylic complexes act as intermediates in many hydrogenation reactions, they have gained a good deal of industrial importance<sup>129</sup>.

Some allylic complexes, as well as some  $\sigma$ -bonded cyclopentadiene complexes, show a remarkable type of isomerism, known as fluxional isomerism. This depends upon the fact that a bond shifts from one carbon atom to an adjacent one freely and rapidly. The individual isomers cannot be isolated, but a good deal has been learned about them through n.m.r. line broadening techniques. The fluxional molecules were not discovered in America, but Americans have studied them and discussed their bonding extensively<sup>130</sup>.

Peripheral members of the metallo-organic family are the remarkable 'sandwich' compounds containing carborane anions such as (3)-1,2- $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$ <sup>131</sup>. The delocalized bonds to the metal in the sandwich comes from a five-membered ring consisting of three boron atoms and two carbon atoms.

### COMPOUNDS CONTAINING METAL-METAL BONDS

In addition to the bonds that hold the atoms together in metals, other metal-metal bonds have long been known. The metal-metal bond in mercury (i) chloride is perhaps the most familiar example, but one recognizes also metal bonds in such compounds as hexaphenyl ditin, the lead-lead bonds in  $\text{Na}_4\text{Pb}_9$  and the bismuth-bismuth bonds in  $\text{Bi}_9^{3+}$ , prepared by Corbett and Rundle (Figure 4)<sup>132</sup> by melting bismuth salts with metallic bismuth.

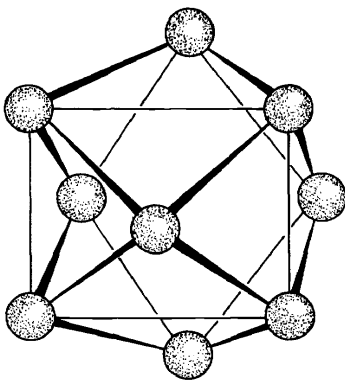


Figure 4. Structure of the  $\text{Bi}_9^{3+}$  ion. Reprinted from *Inorg. Chem.* 3, 1409 (1964).

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During the past decade many metal clusters and other substances containing metal-metal bonds have been prepared and their structures have been determined. Most of these are halides or carbonyls of metals in low

oxidation states<sup>133</sup>. In addition, several acetates of the type  $M(\text{OOC}\cdot\text{CH}_3)_2\cdot\text{H}_2\text{O}$  ( $M = \text{Cu, Cr, Mo, Ru, Re}$ ) have been shown to be dimers, with metal-metal bonds. (In the case of the copper salt, the bond is so long that one may question its existence.) In these, as in many other cases, the metal-metal bond is augmented by bonds to 'bridging' groups.

The anion  $[\text{Re}_2\text{Br}_8]^{2-}$  is remarkable in that it consists of two nearly flat  $\text{ReBr}_4$  units, held together by a quadruple bond<sup>134</sup>. The nature of this bond forces the two  $\text{ReBr}_4$  units to assume an eclipsed relationship. The molybdenum chloride clusters  $[\text{Mo}_2\text{Cl}_8]^{4-}$  and  $[\text{Mo}_6\text{Cl}_8]^{4+}$  form a particularly interesting pair. In each, the molybdenum atoms are enclosed in a cube of chlorine atoms. In the first, the metal atoms are held together by quadruple bonds; in the second, they are bound together in an octahedron with its corners at the faces of the cube (Figure 5)<sup>134a</sup>.

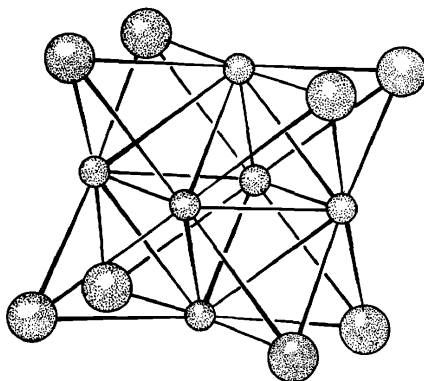


Figure 5. Structure of the  $[\text{Mo}_6\text{Cl}_8]^{4+}$  ion. Reprinted from L. Pauling, *The Nature of the Chemical Bond*. © 1960 Cornell University, Reprinted by permission

Some of the metal carbonyls which contain metal-metal bonds have no other bond between the metal atoms [e.g.  $\text{Mn}_2(\text{CO})_{10}$ ] while others contain bridging carbonyl groups [e.g.  $\text{Fe}_2(\text{CO})_9$ ]. Carbonyls containing two or more different metals are not uncommon [e.g.  $(\text{OC})_5\text{Re}-\text{Mn}(\text{CO})_5$ , and  $\text{Ph}_3\text{Au}-\text{Co}(\text{CO})_4$ ].

Dahl and his students prepared the first metal carbonyl containing a metal cluster and have since prepared several compounds of this class and subjected them to x-ray analyses<sup>135</sup>. Chini in Italy and Marko and Bor in Hungary have also published excellent papers on these substances.

The discovery of the metal cluster compounds opens many new areas for research and demands new and imaginative theories on the nature of bonding.

## NITROGEN AND OXYGEN COMPLEXES

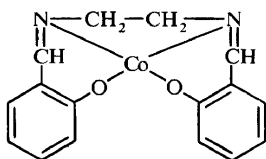
The first synthetic complex containing a nitrogen molecule was reported by Allen and Senoff in Canada, and relatively few chemists in the United States entered this field until very recently. Much research is now going on

in this new area, but a good deal of it has been done so recently that it has not yet been published. Among the synthetic nitrogen-containing complexes, the ruthenium(II) ion  $[(\text{NH}_3)_5\text{RuN}_2\text{Ru}(\text{NH}_3)_5]^{4+}$ <sup>136</sup> is a particularly intriguing one, and it was hoped that the doubly linked nitrogen molecule might be readily reduced to ammonia, but this proved not to be the case.

Von Tarnelen has had remarkably encouraging results in the conversion of nitrogen to ammonia through the reducing power of titanium(II). His review includes not only a description of his own work, but references to that of other methods of fixing nitrogen through the agency of coordination compounds<sup>137</sup>.

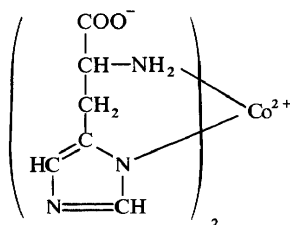
There is intense interest in the structure of nitrogenase, the enzyme which enables bacteria to fix atmospheric nitrogen, and several research groups in America are now attempting to solve its structure. It is known that nitrogenase contains an iron-molybdenum-sulphur complex, but the relationship between these elements is not yet known.

The synthetic oxygen-carrying chelates seem to have been studied more extensively in America than in other countries. During the 1939-45 war, both Diehl<sup>138</sup> and Calvin<sup>139</sup> made detailed investigations of salicylaldimine-cobalt(II) complexes such as that shown in *Figure 6*.



*Figure 6.* bis-(Salicylal)ethylenediamine cobalt(II)

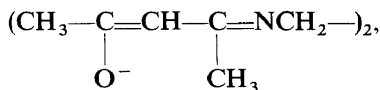
This absorbs and releases oxygen reversibly without changing the +2 oxidation state of the metal. (There is always some irreversible oxidation too.) Hearon and co-workers<sup>140</sup> found that the cobalt-histidine complex



*Figure 7.* Cobalt(II)-histidine complex

similarly absorbs and releases oxygen without changing the oxidation state of the metal (*Figure 7*). Vaska's compound,  $[\text{IrCl}(\text{CO})(\text{P}\Phi_3)_2]$ , likewise absorbs oxygen reversibly<sup>141</sup>.

Two recent papers describe the oxygen adducts of the cobalt complex of the Schiff's base made from ethylenediamine and acetylacetonc,



together with various unidentate bases. The oxygen complexes, which are monomeric, have the formula  $\text{Co}(\text{acacen})-(\text{B})\text{O}_2$ <sup>142</sup>. They are thought to be peroxy adducts of cobalt(III)<sup>143</sup>. It has also been shown that  $[\text{Bu}_4\text{N}][\text{Fe}_2(\text{S}_2\text{C}_2\{\text{CF}_3\}_2)_4]$  reacts with triphenylphosphine in the presence of oxygen to give an oxygen adduct<sup>144</sup>. Platinum(0) complexes have also been shown to form oxygen adducts<sup>145</sup>.

## COORDINATION COMPOUNDS IN BIOCHEMISTRY

Biological phenomena involve coordination compounds in a tremendous number of ways. These compounds have been studied from many points of view—for example, structure, function, reactivity, and mechanism of reaction. Biochemists have studied the functions of these materials for many years, but usually without isolating the compounds. With our increasing knowledge of coordination chemistry and with modern instrumentation, it has been possible to prepare many of the pure compounds and to learn their structures. Even so, the task is a formidable one, for most of the metal-containing molecules of biological interest are extremely large and complex. On this account, some of the inorganic chemists who have been active in this field have worked with model compounds rather than the natural ones<sup>146</sup>. Stability constants of metal-peptide complexes<sup>147</sup>, rates of diffusion of olated complexes<sup>148</sup>, and many other physical properties have been studied extensively in connection with biological phenomena. Among the observations that Diehl<sup>149</sup> has made in his long study of the properties of Vitamin B-12 is the striking one that Vitamin B-12a absorbs oxygen reversibly. Strangely, this has attracted little attention from biologists and biochemists.

Eichhorn<sup>150</sup> has shown that metal ions have the ability to bring about the winding and unwinding of DNA. This was also reported at about the same time by Haia in Japan. This may be of great importance since the winding-unwinding phenomenon is required in all three of the processes that are involved in the transfer of genetic information—replication, transcription, and translation.

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