PREPARATIVE INORGANIC REACTIONS

Volume 1

W. L. JOLLY

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Editor

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PREFACE

The most important information that can be obtained from a chemist who is expert in the preparation of a particular class of compound is the theory, or rationale, behind the preparative methods. The non-expert may possibly use this information in three different ways. He may apply the synthetic principles to the preparation of compounds of the same class which have not yet been prepared. He may apply the principles to the preparation of an entirely different class of compound. If he is imaginative enough, he may, by extending or improving on the expert's ideas, develop a new principle that leads the way to new kinds of syntheses. In a highly developed area of chemistry, the synthetic principles are well enough established so that it is relatively easy to extend them to new compounds. It is difficult to improve on the principles and methods. On the other hand, in a new, undeveloped field of chemistry, the synthetic principles are little more than working hypotheses, to be improved upon as experience is gained.

Another kind of information that can be obtained from an experienced synthetic chemist is a critical evaluation of the various methods that have been used for preparing particular compounds. Such information helps other chemists choose preparative methods which are best suited to their needs.

The chapters in Preparative Inorganic Reactions have been written to provide information of the types discussed above. I believe the authors of Volume 1 have been highly successful in their aims.

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CHAPTER 1

Coordination Polymers

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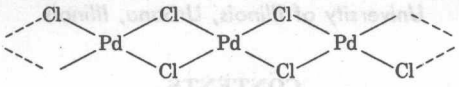
I. INTRODUCTION

For most people, the word "polymer" has come to denote an organic material, each molecule of which has been formed by the union of a large number of small molecules, and which is plastic, flexible, or elastic. In its original use, however, the term does not describe the properties of the material or its composition, beyond indicating that it is formed by the combination of repeating units. If the word is used in this broad sense, inorganic chemistry contains examples of many kinds of polymers. Asbestos and mica are, respectively, linear and sheet polymers, and feldspar, kaolin, and quartz are three-dimensional polymers. If one extends the definition far enough, even ionic, crystalline materials such as sodium chloride and magnesium oxide can be considered to be polymeric. Justification for such an extension can be found in the fact that these substances show some plasticity, but, in general, it is unwise to make a defi-

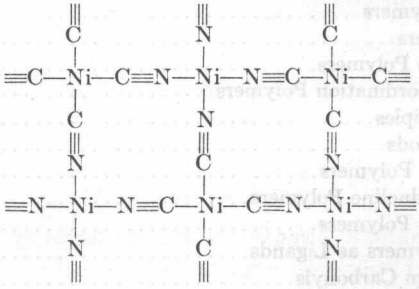
nition too broad, for it then loses its power to correlate closely related phenomena.

A. Cyano Polymers

Among synthetic coordination compounds, there are many examples of polymeric substances, but in most cases, their polymeric nature has been recognized only in recent times. Palladium(II) chloride is an in-



finite linear polymer, nickel(II) cyanide is a sheet polymer (1,2) and the



heavy metal ferro- and ferricyanides, in which the iron shows a coordination number of 6, are three-dimensional, infinite polymers (3). Each of these substances has interesting and useful properties, but, in general, they do not possess plasticity, flexibility, or elasticity. It seems unlikely that these properties will be found in any high degree in purely inorganic coordination compounds in which the valence bonds are rather rigidly arranged and the groups binding the metal atoms together are relatively small.

It is to be noted that in nickel cyanide, alternate nickel atoms are found in different environments, and it might be expected that they would show different properties. Each nickel atom surrounded by nitrogen atoms is capable of combining with two molecules of ammonia, thus expanding the coordination number of the metal to 6; those surrounded by carbon atoms do not show this property. The ammonia molecules in the ammoniated species lie on either side of the polymer plane, thus, holding parallel planes apart and allowing the formation of a clathrate compound containing benzene (1,2). This approaches the empirical composition $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$, but in actual practice, the

material usually contains less than one mole of benzene per mole of nickel (4). The material is readily prepared by shaking a suspension of nickel cyanide in ammonium hydroxide with benzene.

The three-dimensional polymer Prussian Blue or Turnbull's Blue is important because of its deep blue color, which is the result of interaction absorption. Half of the iron atoms in it are in the 2+ state and the rest in the 3+ state. It approximates the composition $KFeFe(CN)_6$, and can be made simply by mixing aqueous solutions of iron(III) with hexacyanoferrate(II) (ferrocyanide) or iron(II) with hexacyanoferrate(III) (ferricyanide). Here again, alternate iron atoms are surrounded by carbon atoms and by nitrogen atoms. Mutual oxidation and reduction of the iron atoms doubtless takes place readily, but one would anticipate that those surrounded by nitrogen would tend to remain in the 3+ state and those surrounded by carbon, in the 2+ state, for coordination with carbon tends to stabilize the lower oxidation states of the metals.

B. Hydroxo Polymers

Another great class of coordination polymers consists of the metallic hydroxides, in which the hydroxyl group serves as the link between metal ions. Titration techniques indicate that these compounds usually contain double bridges (5), but single and triple bridges are also known. Polymerization can be stopped at the dimer stage if suitable blocking groups are present (6)

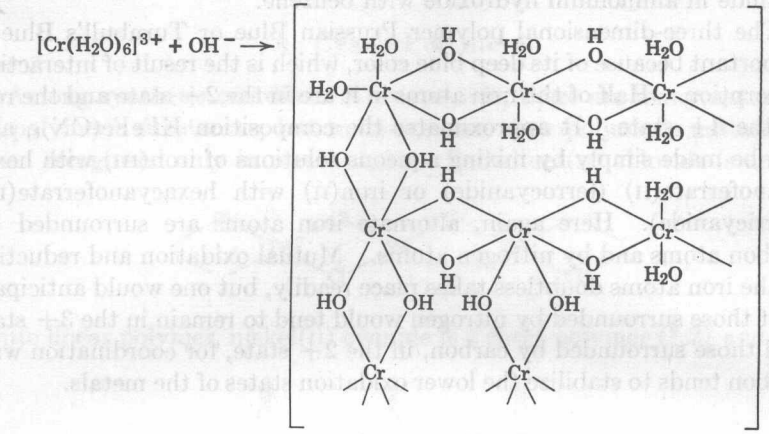
$$[Co(NH_3)_4(H_2O)_2]^{3+} + OH^- \rightarrow [Co(NH_3)_4(H_2O)OH]^{2+} \rightarrow$$

$$[(NH_3)_4Co\begin{matrix}H\\O\\O\\H\end{matrix}Co(NH_3)_4]^{4+}$$

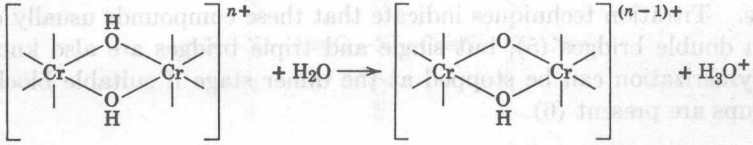
The first step takes place in aqueous solution and the second, when the dry salt is heated to 150°C., at which temperature the water molecule escapes.

In aquated ions containing more than two water molecules, the process of olation can continue to the formation of ions of high molecular weight. This process takes place spontaneously when an aquated metal ion in water solution is treated with a base, and may continue until the product of reaction precipitates from solution. Growth of the polymer can continue even after precipitation, if the material is allowed to stand in the mother liquor, especially at a somewhat elevated temperature. It is also possible to stop the growth of the polymer before it precipitates, and

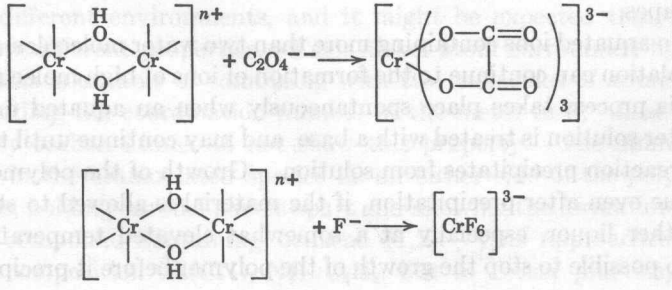
soluble chromium polymers are important in the tanning of leather. The formation of such "olated" polymers is shown schematically:



When an "ol" polymer, in water solution or in the form of a sol, is heated, protons are lost from the ol bridges:



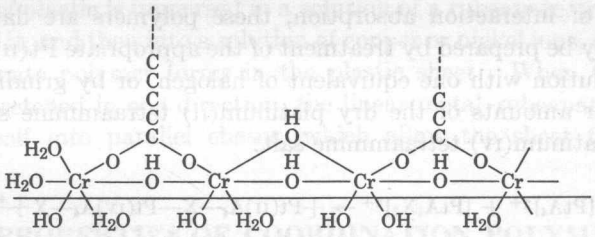
This process, called "oxolation," is only slowly reversed when the temperature is reduced, and the pH of the solution may not return to its original value for several days, the exact time depending upon the nature of the metal ion, the size of the polymer, the degree of oxolation, and other factors. Polymeric structures of this type, both olated and oxolated, can be "broken" by addition of complexing agents which replace the ol or oxol bridges but which cannot form bridges



In the first example, bridge formation is prevented by the strong tendency of oxalate ion to form chelate rings; in the second case, by the small tendency of fluoride to share electrons simultaneously with two metal ions (7).

The phenomena of olation and oxolation were extensively studied some years ago by several investigators, notably Thomas, Stiasny, and Gustavson. The subject has been reviewed by Whitehead (8), Rollinson (9), and Pokras (10). Exact preparative techniques can be found in the references given by these reviewers.

The remarkable water repellent "basic chromic stearate" and "basic chromic acrylate" (sold under the trade names Quilon and Volan) and and analogous hydrophobic, oleophobic basic perfluorocarboxylate (Scotch Guard) illustrate an interesting application of the olated polymers. In the monomeric state, these substances are soluble in the lower alcohols. In use, the solution is spread upon the surface to be treated, and the solvent is allowed to evaporate, leaving a residue which adheres tightly to the surface through the action of some of the ligand groups. When the material is heated, olation takes place, binding the chromium atoms together, with hydrocarbon or perfluorocarbon chains protruding from the surface, and protecting it:



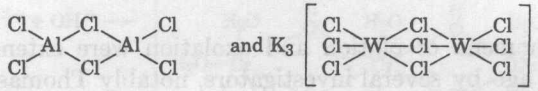
There is good evidence that, in these polymers, the carboxyl groups as well as the hydroxyl groups, serve as bridges.

Schmitz-Dumont (11) has shown that metal ammines can lose protons and ammonia molecules and form polymers which are formally like those generated by olation and oxolation. In these, the bridging members are —NH_2—. Directions for the preparation of some polymers of these types are given in refs. (12) and (13).

C. Halo Polymers

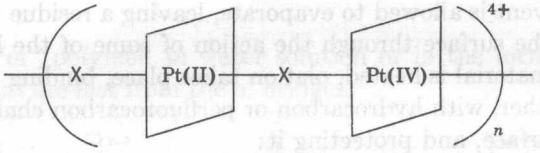
The halide ions show a strong tendency to bridge formation and take part in polymerization. As with hydroxide, double-bridge formation is most common, but single and triple bridges are not unknown. In many

cases, polymerization is limited to the formation of dimers and trimers, such as



but it may proceed to infinite length, as with $PdCl_2$ and $PtCl_2$. Polymer formation in such cases is spontaneous and, generally, it is difficult or impossible to isolate the monomeric species.

The remarkable singly bridged chains of "trivalent" platinum have been studied by x-ray techniques by Brosset (14) and Cohen and Davidson (15). They contain alternate Pt(II) and Pt(IV) atoms, linked together in infinite chains:



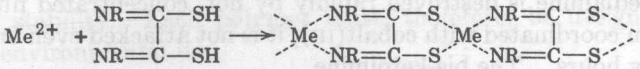
Because of interaction absorption, these polymers are dark in color. They may be prepared by treatment of the appropriate Pt(II) ammine in water solution with one equivalent of halogen, or by grinding together equimolar amounts of the dry platinum(II) tetraammine salt and the dihalo platinum(IV) tetraammine salt:

$$[PtA_4]^{2+} + [PtA_4X_2]^{2+} \rightarrow \text{—Pt(II)}A_4\text{—X—Pt(IV)}A_4\text{—X—}^{4+}$$

Although the fluoride ion shows little tendency to bridge formation, it does so in the remarkable Sn(II)—F_x—Ni(II) complex. Aqueous solutions containing fluoride (in excess) and tin(II) and nickel(II) in widely varying ratios upon electrolysis give an alloy plate containing tin and nickel in approximately equimolar ratios (16). This plate is hard and takes a fine polish; as a result it is being used in England to replace chrome plate. It has been shown (17) that the electrolyte contains a complex containing the two metals in equivalent ratio—the number of bridging fluorides and the complexity of the species are not known. The formation of this ion is particularly interesting in that nickel ion alone does not seem to form a complex with fluoride ion under these conditions (17).

D. Thiooxamido Polymers

Thiooxamide (rubeanic acid) and its *N*-aliphatic substituted derivatives form an interesting series of linear polymers when the organic material, a divalent transition metal ion, and an equivalent amount of a base are mixed in water solution. The polymers are insoluble in water and precipitate as powders.

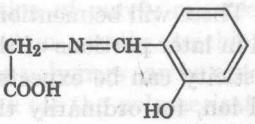


The formation and properties of these polymers have been particularly studied by Hurd and his co-workers at the Mallinckrodt Chemical Works (18). These substances darken upon heating and are of use in duplicating and transfer processes. Some of them (depending upon the nature of the metal and the organic group) are soluble in nonpolar solvents. The rubeanates have been suggested as metal-deactivating agents.

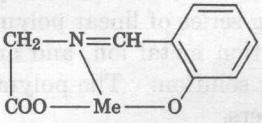
An interesting polymer formed by the action of rubeanic acid and nickel or copper ions has been studied by Amon and Kane (19) who formed it in a layer of an organic plastic. According to their procedure, the sheet of plastic is immersed in a solution of a rubeanate, which penetrates into it, and then into a solution of copper or nickel ions, whereupon the rubeanate polymer forms in the plastic sheet. When the plastic sheet is stretched in one direction, the linear metal–rubeanate polymer orients itself into parallel chains, which allow the sheet to polarize light.

II. PROPERTIES OF COORDINATION POLYMERS

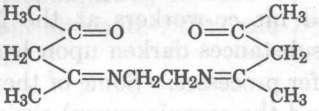
When coordination takes place between a metal ion and a ligand, the properties of both are changed in a variety of ways. It frequently happens that an organic ligand is stabilized towards hydrolysis, chemical reagents, or toward high temperature. For example, hydrolysis of the Schiff base



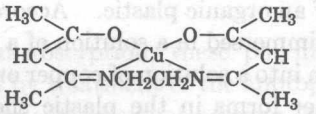
is much more rapid than that of its metal chelates (20)



Ethylenediamine is destroyed rapidly by hot, concentrated nitric acid, but when coordinated with cobalt(III), it is not attacked even on heating for many hours. The bis-ketoimine



is destroyed by heating to moderate temperatures, but its copper complex



is decomposed only slowly at 380°C. (21). Many attempts have been made during the past decade to incorporate these properties (especially heat stability) into plastic organic materials by inclusion of coordinated metal ions into polymer chains. While none of these attempts has been wholly successful, a great deal has been learned, and there is a good basis for believing that valuable plastics of this sort may be obtained eventually.

III. STRUCTURAL PRINCIPLES

In attempts to prepare coordination polymers, a few basic principles must be kept in mind. These will be mentioned briefly here and will be discussed in more detail in later portions of the paper:

(*1*) Little, if any, plasticity can be expected from the immediate environment of the metal ion, for ordinarily the metal–ligand bonds are rigidly fixed in position. Any flexibility or plasticity which the polymer shows must be contributed by the organic portion of the molecule.

(*2*) The presence of a metal ion can protect and stabilize only the organic material which is close to it, so the organic portion of the polymer must be kept to a minimum. It is evident that this principle and the preceding one work against each other, so some compromise composition must be sought.

(*3*) Thermal, oxidative, and hydrolytic stability are not directly related. For example, one coordination polymer may be stable to heat but not to hydrolysis, while another shows good hydrolytic stability but poor thermal stability. Each polymer must, therefore, be designed for a specific environmental use.

(*4*) Even those coordinate bonds which show the greatest degree of covalency are not purely covalent. This means that rearrangements occur more readily than in most organic polymers. Moreover, the metal ion, even when coordinated, still carries a residual positive charge and the ligand (especially if it be an anion), a residual negative charge. These charges exert interchain attractive forces that tend to give rigidity. In the design of coordination plastics, every effort should be made to employ materials that form bonds which are as nearly purely covalent as possible.

(*5*) Compounds which consist of ions are apt to be less plastic than those which are molecular, for interionic forces are strong enough to detract greatly from plasticity.

(*6*) Coordination polymers which consist of a polymeric cation and a simple anion are generally less stable toward heat than those which are purely molecular. Many of the common anions are themselves reasonably strong coordinating agents and compete with the organic ligand for places in the coordination sphere. At elevated temperatures, the competition may favor the simpler material. The common anions which are not good coordinators (NO_3^-, ClO_4^-, etc.) are strong oxidizing agents and, upon heating, destroy the ligand.

(*7*) Chelation is important in increasing stability, and the usual rules concerning ring size and stereochemical effects apply.

(*8*) The relationship between the coordination number and stereochemistry of a metal ion and the nature of the ligand which is attached to it will determine whether the polymer will be linear, planar, or three dimensional.

(*9*) As in the preparation of purely organic polymers, the reactants must be pure and present in exactly stoichiometric ratios; otherwise, only low molecular weight polymers can be obtained.

(*10*) If a solvent is used for the polymerization reaction, it should be one which is not capable of strong coordination to the metal ion, nor should it be capable of generating units which are strong coordinating

agents, e.g., OH^- from solvent water.

With a few notable exceptions, the work which has been done on coordination polymers has been concerned with linear polymers. To obtain such a substance, a combination such as one of the following is required:

(*a*) A bis-monodentate coordinating agent that cannot form a chelate ring, and a metal ion with a coordination number of 2.

(*b*) A bis-bidentate chelating agent in which the two chelating groups do not attach themselves to the same metallic ion, and a metal ion with a coordination number of 4.

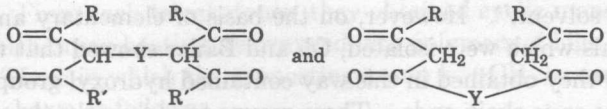
(*c*) A bis-tridentate chelating agent in which the two chelating groups do not attach themselves to the same metallic ion, and a metal ion with a coordination number of 6.

(*d*) A bis-tetradentate chelating agent in which the two chelating groups attach themselves to different metal ions, and a metal ion with a coordination number of 8.

(*e*) A bis-bidentate chelating agent as in (*b*), and a metal ion with coordination number of 6, with two of the coordination positions blocked by nonbridging groups.

In each case, in order to satisfy the principles outlined above, the coordinating agent and the metal ion must be carefully selected. In many cases, a great portion of the work involved in the study of coordination polymers is concerned with the synthesis of the organic part of the molecule. Of the four possibilities, (*b*) has been studied far more than any of the others, chiefly because of ease of synthesis. Examples of this type will be described in detail, and examples of some of the others more briefly.

Most of the polymers formed from metals of coordination number 4 contain beryllium, copper, zinc, or nickel ions. Beryllium offers certain advantages, for it is not subject to oxidation or reduction, its coordination number seems to be invariably 4, and the beryllium–oxygen bond approaches true covalency. On the other hand, the toxicity of beryllium compounds is a serious drawback. The bis-chelating groups which have been most frequently employed are those of 1,3-diketones, 8-hydroxyquinolines, Schiff bases, phosphinates, and α-amino acid anions. In nearly all cases, the bis-chelating agents have been symmetrical, but this has been chiefly a matter of convenience and ease of synthesis. The two chelating groups may be joined together in any of a great number of ways. With the β-diketones, for example, two general structures have been considered:



a and b

where R represents an organic group and Y a connecting unit such as $—CH_2—$, $—CH_2CH_2—$, or $—C_6H_4—$. In some cases, the two diketone groups of bis-chelates of **a** type have been connected directly to each other, e.g., tetraacetylethane.

IV. SYNTHETIC METHODS

A. 1,3-Diketone Polymers

The first studies of bis-diketone polymers were evidently made by Wilkins and Wittbecker (22) and have been continued by Fernelius and his students (23), Bailar and his students (24), Charles and his collaborators at the Westinghouse Research Laboratories (25), Kluiber and Lewis at the Union Carbide Plastics Co. (26), Drinkard, Ross, and Wiesner (27), and others. In most of the early work, attempts were made to prepare polymers by the same techniques which are used to prepare monomeric complexes of 1,3-diketones. Oh and Bailar (24) say: The method "consists of mixing the ketones and a soluble metal salt in the proper proportions in a water–organic solvent mixture, and adjusting the pH until the chelate precipitates. It is necessary to add an organic solvent such as alcohol, dioxane, or dimethylformamide because of the insolubility of the ligand in water. The success of this method depends upon pH, rate of addition of the base, rate of stirring, temperature and reaction time.

"In some cases polymers were obtained simply by the addition of an excess of an aqueous solution of metal acetate to a dioxane solution of the bis-(β-diketone). The highly insoluble precipitate was purified by extraction with water followed by an organic solvent such as alcohol, acetone, or benzene.

"In the cases in which immediate precipitation did not occur, the pH was adjusted by addition of ammonia or urea. When no precipitation occurred in the reaction mixture even after standing for a long time, the reaction mixture was evaporated slowly in vacuo and the residue was collected. The residue was purified by extraction with water followed