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SOME TRENDS IN INORGANIC CHEMISTRY

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One must be very brave or very foolish to attempt to present a paper on "Trends in Inorganic Chemistry", first, because there is so much material to be reviewed and secondly, because one must not only discuss what has happened, but must also predict where the current trends are leading us.

Inorganic chemistry has always been an important branch of science, but until a generation ago, it was greatly overshadowed by organic, analytical and other branches of chemistry. In the Western world, "Der Zeitschrift fur anorganische und allgemeine Chemie" was the only journal of any significance which was devoted entirely to that subject, but within the past few years at least ten new journals devoted to various aspects of inorganic chemistry have started publication. Some of these are specialized, and their titles give some hint of the trends in inorganic chemistry: "The Journal of the Less Common Metals", "Bioinorganic Chemistry", "The Journal of Organometallic Chemistry", "The Journal of Fluorine Chemistry", "The Journal of Solid State Chemistry", "The Journal of Catalysis", and "Catalysis Reviews".

It is evident from these titles, that inorganic chemistry has greatly broadened its scope and is overlapping heavily with organic and biochemistry. At the same time, parts of it have become highly specialized and a good many inorganic chemists devote their entire efforts to the chemistry of a single element, e.g. fluorine or a group of elements, such as the lanthanides or the actinides.

This great surge of research in inorganic chemistry has been brought about in large measure by the invention of new types of equipment for IR and UV spectroscopy, NMR, Mössbauer spectroscopy, electron spin spectroscopy and computers which enormously simplify the interpretation of X-ray data.

The area of inorganic chemistry which has, perhaps, shown the most rapid growth is organometallic chemistry. This began a century and a half ago with the discovery of the platinum—olefin complexes by Zeise. Other important aspects of it were started by Frankland's work on organo zinc compounds and Grignard's discovery of the famous reaction which bears his name. The latter two have been of interest chiefly to organic chemists, but the metal—olefin compounds, because of their similarity to Werner complexes, are considered to be inorganic. The metal carbonyls, ferrocene and its analogues, and most other types of organometallics are generally considered to be inorganic, though organic chemists use them freely in synthetic and catalytic studies.

The metal carbonyls have been studied in great detail [1] and their structures and reactivities are well-known. However, there are so many of them, and their chemical behavior is so varied, that there is still a great deal to learn about them. We do not understand, for example, why the replacement of carbon monoxide from the iron carbonyls stops short of complete replacement

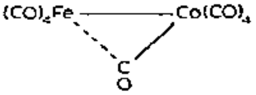
$$Fe(CO)_5 + 6\ C_6H_5N \rightarrow [Fe(C_6H_5N)_6][Fe_4(CO)_{12}] \qquad \text{(ref. 2)}$$

$$Fe_3(CO)_{12} + 3\ \text{o-phen} \rightarrow [Fe(\text{o-phen})_3][Fe_2(CO)_8] \qquad \text{(ref. 2)}$$

or why the elimination of tetrahydrofuran from [$Fe(CO)_4$THF] leads to the trimeric product

$$3[Fe(CO)_4THF] \rightarrow [Fe_3(CO)_{12}] + THF \qquad \text{(ref. 3)}$$

The mechanism of these and similar reactions still needs to be explored. The structure and bonding of the polynuclear, bridged carbonyls are particularly interesting and should receive increased study, not only because they offer new avenues of chemical thought, but also because they may serve as catalysts and as the bases for synthetic work. As Cotton has pointed out [1], in molecules containing carbon monoxide bridges, there are nearly always metal—metal bridges, too. However, no such bridges can form if the metal atoms are too far apart or if suitable orbitals are not available. Many of the polynuclear carbonyls are in equilibrium with their monomers; others have a highly fluxional character, so they cannot be assigned fixed structures. In still others, the number of electrons surrounding the metal atoms is not that required by the "effective atomic number" concept, and assumptions must be made to account for the existence of such carbonyls, for example the semi-bridging structure [1]



All of these properties, and many more, will demand the attention of chemists for a long time to come.

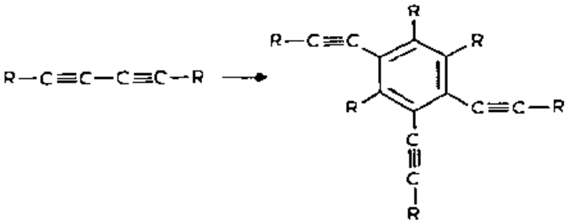
The metal carbonyls have achieved great importance in the catalysis of organic reactions, the most important, from an industrial standpoint, being the oxo reaction

$$RCH{=}CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} RCH_2CH_2CHO$$

and the preparation of acetic acid from methanol and carbon monoxide

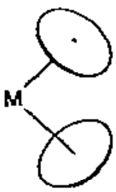
$$CH_3OH + CO \xrightarrow{Co_2(CO)_8} CH_3COOH$$

Another interesting example, though not now of industrial importance, is furnished by $Ni(CO)_2(P\Phi_3)_2$, which converts 1,3-diacetylenes to cyclic products [4]

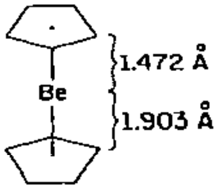


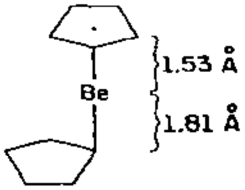
There are other reactions, both carbonylations and others, which are catalyzed by metal carbonyls, and they may well occupy an increasing role in chemistry.

The metal—cyclopentadiene complexes continue to attract a great deal of attention, and new types of them are being found even yet [5]. The pentahapto structure proposed for ferrocene in 1951 is valid for many of the simpler compounds, though in the tin and lead compounds (at least in the vapor phase) the two cyclopentadiene rings are not parallel [6].

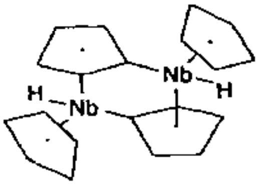


In those which are parallel, the rings may be staggered (Fe, Co, Mg) or eclipsed (probably V, Cr, Mn, Ni, and some others, though the staggered form cannot be ruled out). The beryllium complex is of special interest. The two organic rings are parallel, but in the vapor phase, they are not equidistant from the metal atom. The beryllium atom shows a dynamic behavior, alternating its position between the rings [7,8]. The solid state structure is not fully understood. Either one of the rings is pentahapto, and one monohapto, or both are pentahapto with the rings offset from each other by 1.20 Å. These peculiarities are attributed to the small size of the beryllium atom [7b,8], or the relatively large number of electrons which is available [9].

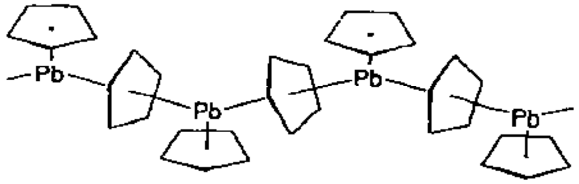




Di- and tri-haptocyclopentadienyl compounds are known, sometimes carrying other organic groups than cyclopentadiene, e.g. dihapto $Al(CH_3)_2Cp$ [10]. Dimeric compounds are known also, niobocene being a good example [11].

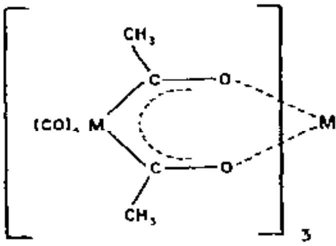


and the lead compound, which in the solid phase forms polymeric, orthorhombic crystals [12].



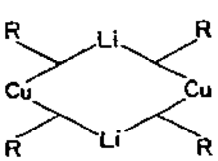
Cyclopentadiene complexes containing more than two Cp rings per metal atom are known, though in some cases their structures are not well understood. $MoNOCp_3$ is thought to contain one monohapto ring and two rings which are between tri- and penta-hapto [13]. The structure of cyclopentadienyl zirconium, $ZrCp_4$, is still in doubt, as the reported structure does not agree with those for $HfCp_4$ and $TiCp_4$, each of which contains two monohapto and two pentahapto rings [14].

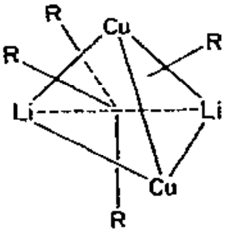
The union of several carbon monoxide molecules and a metal often gives a group which has semi-organic character, and this may be used in the synthesis of interesting and unusual compounds. Lukehart and co-workers [15] have prepared several compounds of the type $(CO)_4M(COR)_2$ (M = Mn or Re) which are isoelectronic with β-diketones. From these, they have made complexes with aluminum and gallium (M') which do indeed closely resemble the β-diketone complexes.



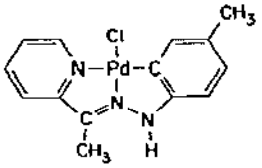
M = Mn or Re
M' = Al or Ga

There are, of course, many other organometallics which are extremely interesting. For example, the structures of the lithium organocuprates, which have become important reagents, are not well understood [16], but evidence has been advanced for such formulae as are shown below.



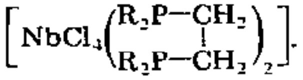


In a very recent paper, Nonoyama [17] has described an interesting palladium compound, which is formed readily at room temperature, in 83% yield,



from the hydrazone and lithium tetrachloropalladate. The bromo compound was prepared in the same way, and the iodo compound by metathesis of the chloro complex and lithium iodide. The surprising ease of formation and the stability of these substances are sure to attract other investigators.

Nyholm once commented that in recent years, we have greatly simplified the study of inorganic chemistry. It used to be that the new student had to memorize the valencies of the various elements, but now he can safely assume that all metals have all of the possible valencies. Vaska's compound, which contains iridium(I), is widely known, and analagous compounds are no longer surprising. We are somewhat surprised, however, to read of hexafluorides of arsenic, antimony, chlorine and bromine [18] and of platinum(V) and palladium(V) [19]. Some other interesting examples are found in a recent paper on $Cp_2Nb(CH_3)_2$ and $(CH_3Cp)_2Ta(CH_3)_2$ [20]. Research on such substances will certainly continue, for they will find wide use. The unusual, unreactive $NbCl_4$ was prepared by reduction of $NbCl_5$ in the presence of an excess of acetonitrile, which gave the soluble $NbCl_4(CH_3CN)_3$ [21]; this was readily converted to $NbCl_4(THF)_2$, which is soluble and quite reactive, and was easily converted to the six-coordinate $[NbCl_4(PR_3)_2]$ and the eight coordinate

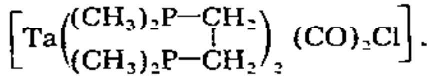


$$\left[NbCl_4\begin{pmatrix} R_2P-CH_2 \\ | \\ R_2P-CH_2 \end{pmatrix}_2\right].$$

Moody and Ryan have recently prepared, by the reduction of UCl_4 in excess THF [22], a soluble form of $UCl_3(THF)$ which was easily desolvated to UCl_3. This simultaneous reduction and coordination may turn out to be a general technique for the preparation of elements in unusual oxidation states. A somewhat different aspect of it has been described by Hofmanova' et al., who used electrolytic reduction [23].

Even fractional valencies are described in the recent literature, and are discussed in a recent review [24]. Complexes of the types $K_2Pt(CN)_4Br_{0.3}(H_2O)_x$, $K_{1.74}[Pt(CN)_4]$ and $[Pt(C_2O_4)_3]^{-1.64}$ are readily prepared and have interesting electronic properties.

Coordination number five and its stereochemistry, almost (but not entirely) unknown twenty years ago, has now been illustrated by scores of examples and needs no discussion here [25—28]. Seven coordination, though not yet common, has been well established, and its stereochemistry is being explored. This has been discussed in detail by Drew [29]. Chemical methods of structure determination are not generally applicable, for complexes of high coordination number are readily distorted and isomeric forms tend to convert readily into each other. However, X-ray, NMR and other physical techniques can often give unequivocal structural information. This has been discussed by Datta and Wreford [30], who illustrate the point by a discussion of the seven-coordinate complex



$$\left[\mathrm{Ta}\begin{pmatrix}(CH_3)_2P-CH_2\\ \quad\quad\quad\quad | \\ (CH_3)_2P-CH_2\end{pmatrix}_2(CO)_2Cl\right].$$

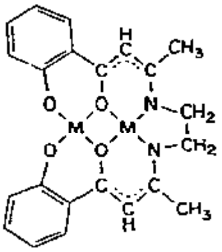
Their synthesis of this interesting compound was begun with a solution of $TaCl_5$ and the ligand in a mixture of benzene and THF. Upon reduction, this gave successively $TaCl_4 \cdot L_2$ and $TaCl_3 \cdot L_2$, and upon reductive carbonylation $TaL_2(CO)_2Cl$ and finally, $Na[TaL_2(CO)_2]$.

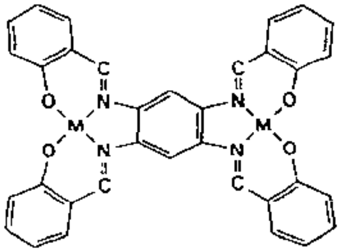
Bioinorganic chemistry is closely related to organometallic chemistry, though in most biochemicals the metal is attached to nitrogen or oxygen rather than directly to carbon. Not only is the chemistry of metals in biological systems intrinsically interesting, but since everyone is interested in life and health, this is an area of inorganic chemistry which will certainly win increasing attention. The work of Williams, Holm, Eichhorn, Collman, Vallee, Gray and many others is so well known that it need not be reviewed here. The subject is so vast that it fills many books [31].

The mechanism of nitrogen fixation, to which Chatt has contributed so greatly, is known to involve both iron and molybdenum and models have been synthesized in efforts to duplicate the natural enzyme [32], but the problem has not yet been solved. Because of the great interest in biological nitrogen fixation, the study of molybdenum occupies a special place in bioinorganic chemistry. The chemistry of molybdenum is complex, as the metal shows all of the formal oxidation states from —2 to +6, and coordination numbers from four to eight. The chemistry of molybdenum has been ably reviewed by Stiefel [33].

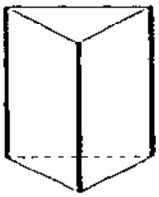
Rosenberg's work on the use of platinum compounds in the treatment of cancer has stimulated a great deal of research, and doubtless will continue to do so. The inorganic chemistry involved in the study of these complexes is simple, embracing only the preparation of the uncharged *cis*-platinum(II)diammine dihalides and derivatives, but undoubtedly, it will eventually involve the synthesis of more complex diammines, as efforts to obtain substances of higher efficacy and lower toxicity continue [34].

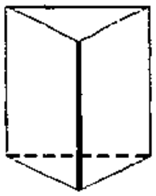
Also related to bioinorganic chemistry is the work on macrocycles, begun some years ago by Curtis and by Busch. Synthetic methods have now been developed so that a great variety of macrocyclic complexes can be prepared. The dinuclear compounds prepared by by Hendrickson and co-workers [35], Fenton et al. [36], and Merrell and co-workers [37] are somewhat similar to these, in that the metal ions are completely surrounded by an array of chelate rings. The dinuclear complexes are of interest because of the interaction of the magnetic moments of the metal ions.





Stereochemistry, long the basis of much of the work on coordination chemistry, is still important, but is being attacked in new and different ways. Werner's simple concepts are being refined and expanded by the use of exact physical methods. Some new aspects of the stereochemistry of six coordination have been discussed in detail by Kepert [38], who has shown that purely octahedral structures are not common, but are distorted by ligand—ligand repulsions, Jahn—Teller effects, steric crowding, and perhaps other causes. Six coordinate trigonal-prismatic structures, not even suspected until a few years ago, are not at all uncommon, nor are structures between the octahedral and trigonal prismatic, which are well known. Bidentate ligands can give complexes which are either octahedral or prismatic, the latter being of two isomeric forms.


A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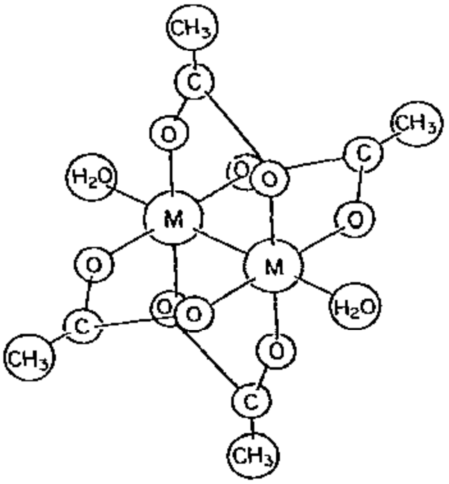
Those in which the normalized bite is below ca. 1.3 tend to give complexes of type A, in which the longer edges are between the ligands, while those in which the normalized bite is larger tend to give complexes of type B, the longer edges being spanned by the ligands. Complexes of the type *trans*-[M(AA)$_2$c$_2$] form octahedra. If the bidentate ligand has a large normalized bite, the octahedron will be quite regular, but if the bite is small, the figure will be distorted and may even become a skewed trapezoidal bipyramid.

Metal clusters constitute an extremely interesting group of compounds which is attracting increasingly wide attention, both from those who are interested in the theory of bonding, and those who work in catalysis. The simplest of metal clusters consists of those which contain only metal atoms or ions; for example, Cd_2^{2+}, Te_4^{2+}, and Bi_9^{5+}. Corbett has studied these extensively, and has written a review on them [39]. It is unfortunate, I think, that there has not been more work in this area. The metal acetate monohydrates, $M(OOCCH_3)_2 \cdot H_2O$, form an especially interesting family. They are dimeric, the two metal ions being held together, in part, by the bridging acetate groups.



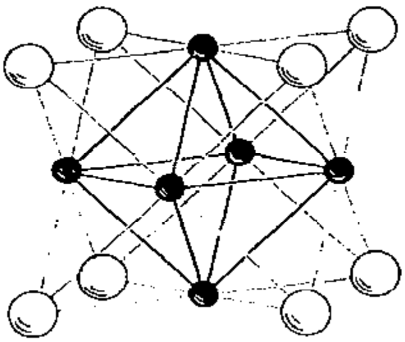
The intermetallic distances vary considerably in these compounds, as shown in Table 1. In the copper(II) compound, the intermetallic distance is so great that there probably is no bond; in molybdenum(II) acetate, on the other hand, the metal atoms must be squeezed together very tightly.

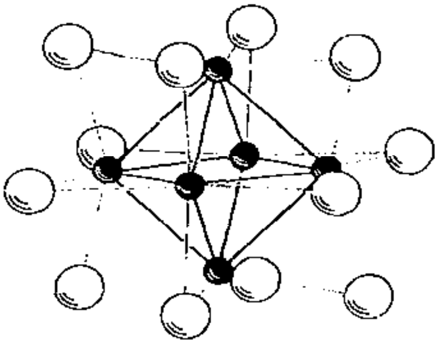
In the ions $Mo_6Cl_8^{4+}$ and $Ta_6Cl_{12}^{2+}$ the metals form octahedra, each metal atom being attached to four others. The apices of these octahedra are in the centers of the faces of a cube. In the molybdenum compound, the chlorine atoms are at the cube corners; in the tantalum compound, at the centers of the cube edges.

TABLE 1

Metal—metal distances in some acetates (Å)

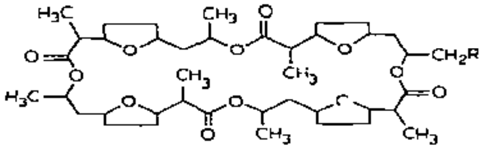
	Metal—metal distance	Pauling's single bond radii (× 2)
Cu^{2+}	2.64	2.34
Cr^{2+}	2.36	2.36
Rh^{2+}	2.45	2.50
Mo^{2+}	2.11	2.60



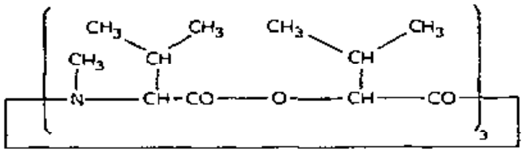


Metal—metal bonding is particularly common in the carbonyls. In some of these, such as $Mn_2(CO)_{10}$, there seems to be no bonding except that between the two metal atoms, whereas in others, such as $Fe_2(CO)_9$, some of the carbonyl groups serve as bridges. The entire subject has been reviewed by Chini et al. [40]. Sulfur compounds also tend to form metal—metal bonds; this topic has been reviewed by Fackler [41].

In discussing trends in inorganic chemistry, mention of the crown ethers should certainly be made. Some naturally occurring antibiotics are cyclic ethers



R = H Nonactin
R = CH_3 Monactin



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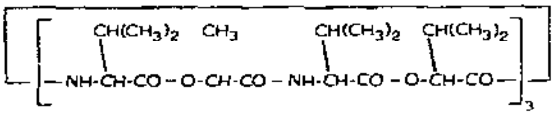
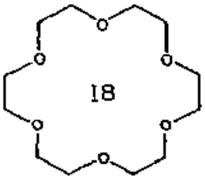
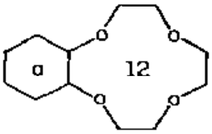


Valinomycin

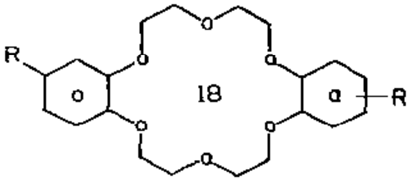
and it has long been known that they can sequester metal ions, especially those of the alkali and alkaline earths. Pederson [42] prepared the first synthetic cyclic ether in 1967, and since that time they have been the subjects of much attention, with respect to synthesis, ring size, bonding and utility.

These cyclic ethers can be prepared with a wide variety of ring sizes and can thus be made to differentiate between metal ions of different radii. Best known are those which contain six oxygen atoms in rings of eighteen members, the so-called "18—6" crown ethers. The ether ring may be the only ring in the molecule, or it may be attached to one or two benzene or cyclohexane rings.



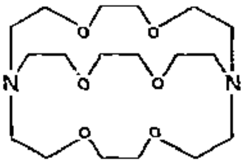


a = BENZO
a = CYCLOHEXYL

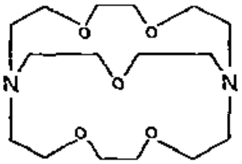


a = BENZO R = H
a = BENZO R = t-BUTYL
a = CYCLOHEXYL R = H
a = CYCLOHEXYL R = t-BUTYL

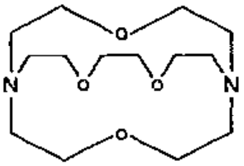
The presence of cyclohexane rings greatly increases the solubility of the complexes in non-polar solvents, and allows purely ionic materials like potassium permanganate to be dissolved in benzene, in which it acts as a strong oxidizing agent. The oxygen atoms in the cyclic ether rings can be replaced in part by sulfur or nitrogen atoms. In the latter case, multiple fused rings can be formed. These substances are called cryptates, and are sold commercially under the trade name "Kryptofix".



Kryptofix 222
K^+



Kryptofix 221
Na^+



Kryptofix 211
Li^+

Stability constants $\log_{10} Ks$ of the alkali cations in H_2O at 25°C

Kryptofix	Interstitial radius	Cation (ionic radius)				
		Li^+ (0.86)	Na^+ (1.12)	K^+ (1.44)	Rb^+ (1.58)	Cs (1.84)
222	1.4	<2	3.9	$\boxed{5.3}$	4.3	<2
221	1.15	2.5	$\boxed{5.3}$	3.9	2.5	<2
211	0.8	$\boxed{4.3}$	2.8	<2	<2	<2

The structures of some of these materials are shown above, illustrating their selectivity for various alkali and alkaline earth ions.

Unfortunately, the synthesis of crown ethers and cryptates is difficult and they are too expensive to use in large amounts. They are being used in some applications, however. If and when the price is lowered, they will certainly find many uses.

The boranes have long been of theoretical interest because they seemed to early workers to violate the rules of bonding. Chemists have now reached general agreement on this score, and only a few people continue to work in that area. Brown is an outstanding exception and has done brilliant work, especially in his study of the reactions of organic boranes [43]. The borohydrides are of great practical interest, but the focus of theoretical chemistry in this area has now shifted to the carboranes, which are of both theoretical and practical interest. The carboranes have the general formula $[(CH)_a(BH)_bHq]^{-c}$, and fall into three homologous series. If $a + q + c = 2$, the compound has a closo structure; if $a + q + c = 4$, it has the nido structure, and if $a + q + c = 6$, the arachno structure. In some cases, isomers are known [44].

The study of catalysis, which is an extremely important part of inorganic chemistry, has undergone great changes in recent years. This has been made possible by the development of instruments for the measurement of surface properties [45]. As our knowledge of adsorption and desorption processes increases, we learn more and more about the kinetics of reactions on surfaces. Homogeneous catalysis, too, is undergoing rapid change, as our knowledge of the kinetics of very fast reactions increases. The two areas, homogeneous and heterogeneous, are being combined in some cases, with the fixing of homogeneous catalysis on solid surfaces [46]. Because of its immense practical importance, physical and chemical research on inorganic catalysts will certainly continue at an accelerating rate.

Finally, another area of inorganic chemistry that is growing in importance is photochemistry. The yields in most photochemical reactions are very small, so synthetic procedures are not yet widely used, but as more is learned about the subject, this may change. Wrighton's recent review [47] on mechanistic aspects of photochemical reactions of coordination compounds discusses the subject from several angles and in detail.

These, then, are the inorganic areas that I think will develop rapidly in the reasonably near future. Doubtless, I shall be proved wrong in some cases; areas that I think will be most important will prove not to be so, and some that I have neglected may become tremendously important. There are enough of them however, that one can be sure of one prediction, that inorganic chemistry will continue to grow in interest and importance.

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