INTRODUCTION

1. What are chelates?

It is possible for coordination to take place between two atoms which already form part of the same molecule. In that case, the product must contain a ring and such substances have been called by Morgan and Drew(1) by the convenient name of CHELATE compounds. The term is derived from the Greek word χηλὴ (=a crab's claw), referring to the great claw of the lobster and other crustaceans and is applicable to these ring systems because of the calliper-like character of the associating molecules. The formation of these rings may be considered to involve either primary or secondary valency. Morgan and Drew applied the term to rings containing coordinating links(secondary valencies), but the expression chelate ring is now used to cover all the three types of the rings, i.e. rings formed by two primary valencies, by one primary valency and one secondary valency and by two secondary valencies. Hence the following definition of chelate compounds: The term CHELATE is used to designate those cyclic structures which arise from the union of metallic atoms (or hydrogen) with organic and inorganic molecules. (When hydrogen is involved in coordination, the bond is usually known as hydrogen bond or H-bond. The chelates containing metal atoms are often termed as metal chelates to distinguish them from "hydrogen chelates" where hydrogen is involved in ring formation.)

2. Existence of a chelate ring.

The existence of a chelate ring was, for a long time, unrecognised, since the molecule could be represented as an open chain without assuming coordinate link; the idea of ring structure in ethylene diamine complexes runs subconsciously through the early pages of Werner(2;3) without being definitely expressed. In 1901, however, Werner(4) specifically assigned a cyclic structure to platinum acetonylacetonates. Other cyclic structures were soon suggested for copper glycinate by Ley (5) in 1904 and for nickel dimethyl glyoximate by Tschugaeff (6) in 1907. The possibility of ring structures formed by coordinate links was further suggested by Tschugaeff (7) for the metallic compounds of biuret and similar substances and by Werner (8) for the compounds formed by dyes with the mordants. These are a peculiarly stable group of compounds, probably because the normal covalencies hold the molecule together even if the coördinate link breaks.

3. Evidence for the existence of the chelate rings.

The most important facts upon which the existence of the chelate rings has been based are:

(a) Thousands of coordination compounds are known in which the coordination numbers of the metals involved are invariably 4 or 6 and yet only 2 or 3 molecules of organic compounds containing two associating structures unite with such metals. Therefore, if all the coordinate positions are to be occupied and the compound is to be assumed to be monomolecular, the linking of all 4 or 6 units with consequent ring formation must occur.

(b) Reactions which normally reveal the presence of certain metals, fail in solution of their complex salts, thus indicating the absence of simple ions of the metal. This is further confirmed by conductivity and migration measurements which prove the complex to be a non-electrolyte, anion or cation, assuming the chelation to occur.

(c) Chelate compounds are saturated and are generally incapable of adding further coordinating addenda.

(d) On the basis of chelate structures certain isomers are predictable and such predictions have been realised in many instances.

(e) Chelation is seen in certain cases to yield asymmetric structure and proof of this is found in the resolution of many metallic compounds of this type.

(f) Functional groups which are involved in chelation are found to be non-reactive.

(g) Chelate compounds are formed only with those organic molecules which have functional groups in such positions as to yield rings of from 4 to 7 members.

(h) Functional groups responsible for ring formation take part equally in reactions which result in opening of the ring.

4. Chelate rings and "Organic" rings.

Chelate rings differ from the ordinary isocyclic and heterocyclic rings of organic chemistry in containing coordinate links in most cases and this form of the link is always a source of instability, since the products of its rupture are, in general, more stable than those formed by breaking of a normal covalent link. This comparative instability is shown by the fact that while normal rings with any number of atoms from 3 to 18 are known, chelate rings never contain less than 4 and very rarely more than 6. This limitation of size is evidently due to the effect of strain to which the coordinate link renders these rings peculiarly sensitive.

5. Metal chelates and salts.

Sidgwick (9) in his study of ionic and covalent linkages, has tried to differentiate between a salt and a metal chelate. High m.p., solubility in water and non-solubility in organic solvents are considered to be the characteristics of a salt. Thus, sodium derivative of benzoyl acetone might be either a salt or a chelate compound. Sidgwick and Brewer (10) have found that it chars on heating without melting, dissolves readily in water and is insoluble in benzene and toluene. They assumed that as all these properties are those of a salt, the sodium derivative has the formula of a salt. If it is recrystallised from aqueous alcohol, it takes up two molecules of water. This might be " the water of crystallisation" in the sense that it was attached to sodium ion. If so, the solubility of the hydrated compound should be of the same order as that of the anhydrous salt. But the hydrate is found to dissolve in toluene. This is a clear proof that it is not an ionised but a covalent(chelate) compound.

A rather less obvious example is that of acetyl acetonate of dimethyl thallium (11). The compound has a fairly low m.p., can sublime easily in vacuo and is readily soluble in benzene. All these properties make it clear that the molecule is covalent and the chelate formula is correct. It is found, however, to dissolve readily in water; chelate formula has no associating groups to account for this solubility and the only possible explanation is that the molecule which alone, and in benzene, has a chelate structure changes in water into the ionised form.

With the metallic compounds, the methods by which the presence of chelate rings can be detected consist mainly in showing that the metal is not present as a simple ion; either the whole molecule is covalent, or if it is ionised, then the metal atom is part of a complex ion which includes chelate group.

6. Metal chelates and metal complexes.

When a metal ion combines with an electron donor, the resulting substance is termed a complex or a coordination compound;if the substance combines with the metal through two or more donor groups so that one or more rings are formed, the resulting structure is said to be a chelate compound or a metal chelate.

Complexes and chelates are formed by nearly all the metals of the periodic system. Although the number of known chelating and complexing agents is very large, the donor atoms which undergo combination with the metal are restricted to the strongly nonmetallic elements of groups V and VI of the periodic table;of these,nitrogen,oxygen and sulphur are the common examples.

Some of the chemical and physical properties of metal chelates resemble those of the simple complexes and differ only in a qualitative way. Other properties,on the other hand,are fundamentally different and may be used for identifying the chelates and for distinguishing them from complexes.

7. Metal chelates and inner complex salts.

In 1904, Ley (5) reported a number of amino acid cyclic complexes of metals,which he named inner complex salts. The term 'inner' indicated the ring formation; the term 'complex' indicated the presence of secondary or coordinate bonds; and the term 'salt' was used to denote the primary bond formation between the metal and the negative carboxyl group. Inner complexes have received considerable attention as a special class of chelates because of their unusual and striking properties which are as follows:

(a) very low dissociation (low electrical conductivity of solutions),

(b) frequently insoluble in water and soluble in nonpolar solvents, and

(c) colours which differ greatly from those of the normal salts of the metals.

Ley apparently intended that inner complexes be restricted to non-ionic substances. According to this, inner complexes would be formed when the coordination number and charge of a metal ion are exactly balanced by the number of the donor groups and charges, respectively, of the chelating ions with which it combines. The most common inner complexes are formed by bidentate chelating agents having one replaceable hydrogen with metals, the coordination numbers of which are exactly twice the principal valencies.

It was observed that chelating agents may contain more than two functional groups through which they may be linked to the metal atoms. With the discovery of such compounds, Morgan (12) devised the terms tridentate, quadridentate, etc., literally meaning three-toothed, four-toothed, etc. In tridentate chelates the chelating agents will have three functional groups through which they will be linked to the metal atom and thereby two rings will be obtained. Thus polycyclic ring compounds will be formed in the case of polydentate chelates. According to this nomenclature, the chelating agents having two functional groups can form bidentate chelates (unicyclic rings).

Considerable work has been done on tridentate chelates (bicyclic ring compounds), but little is known about quadridentate, pentadentate and sexadentate chelates. Mention may be made here of the work done by

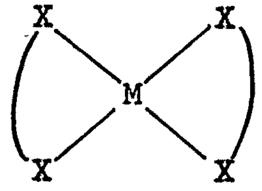
(a) (i) Morgan and Main-Smith (12), (ii) Stackelberg and Freyhold (13), (iii) Calvin et al.,(14), (iv) Dubsky and Sokol (15) and (v) Ray, et al., (16) on quadridentate chelates (tricyclic ring compounds), and

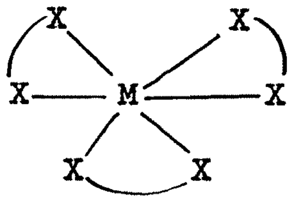
(b) Dwyer and Lions (17) on sexadentate chelate compounds (pentacyclic ring compounds).

A schematic representation of the types of chelates that may be formed as a function of the coordination number of the metal and the number of coupling groups in the organic molecule is shown as follows:

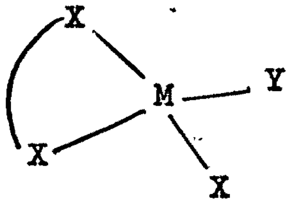
coordination No.4 coordination No.6

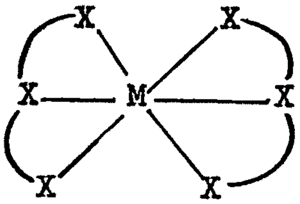
bidentate



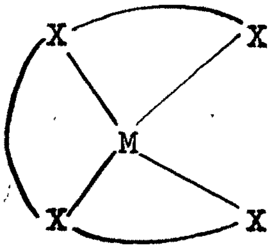


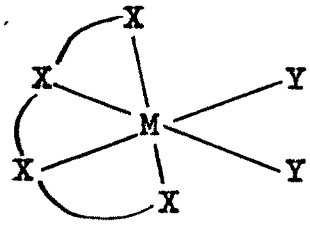
tridentate





quadridentate





9. Types of chelate rings.

According to Diehl (18), the classification of chelate rings on the basis of the number of the functional groups present in the chelating agent and taking part in chelation will be:

Class-1.Unidentate: A: either acidic or coordinating groups; (groups held in the coordination sphere) Obviously, complexes with unidentate ligands would not involve chelation.

Class-2.Bidentate: A: two acidic groups;
B: one acidic group and one coordinating group;
C: two coordinating groups;

Class-3.Tridentate: A: three acidic groups;
B: two acidic and one coordinating groups;
C: one acidic and two coordinating groups;

D: three coordinating groups;

Class-4. Quadridentate

A: four acidic groups;

B: three acidic and one coordinating groups;

C: two acidic and two coordinating groups;

D: one acidic and three coordinating groups;

E: four coordinating groups;

and so on.

Of these, thousands of members of class-1 are known; numerous examples of class-2 exist; a few examples are known of class-3. The knowledge about subsequent classes is very scanty.

Among all classes the valency of the complex radical is equal to the valency of the central metal atom minus the number of the primary valency groups held in the coordination sphere. The successive replacement of simple coordinating groups in the coordination sphere by acidic groups leads to a series of compounds the complex ions of which have successively changing ionic charges.

It may be mentioned here that Sidgwick(19) has proposed a classification of chelate rings into three types, which is based on the character of the bonds present in the cyclic system. Rings in which the coordinating links become identical with a normal covalent bond as a result of chelation are designated as type -A. Rings containing one coordinating bond and one covalent bond are designated as type-B and those containing two coordinate links as type-C. It should be pointed out, however, that the three types are not always sharply differentiated and there is evidence that in the liquid state and in solutions the chelate structure exists in equilibrium with a non-chelate system.

9(a). Chelate rings of class - 2.

Rings of type-A are formed by the replacement of two hydrogen atoms of a dibasic acid by a metal atom. These structures are usually quite stable and in addition to the common 5-membered and 6-membered rings, may contain cycles of 4 and 7 members, which are found only infrequently in other types of chelate rings. The most common functional groups (in a compound) which are capable of forming such rings are

(1) -COOH and -COOH
(2) -COOH and $-SO_3H$
(3) -COOH and -OH
(4) -COOH and -SH
(5) $-SO_3H$ and $-SO_3H$
(6) -OH and -OH
(7) -OH and -NOH
(8) $-CONH_2$ and $-CONH_2$.

In systems of type-B, an atom is bound in the ring on one side by a normal covalent bond and on the other by a coordinate link. Rings of this type are usually less stable than those of type -A, and they always contain 5 or 6 members. Structures most frequently found are 5-membered rings containing one double bond and 5-and 6-membered rings containing two double bonds. The conjugated, 6-membered rings of this class are perhaps the most common of all chelate structures. Atoms, occurring in these rings, other than a metal or a hydrogen, are carbon, nitrogen, oxygen and occasionally sulphur. Since the metal is not linked to carbon, and sulphur is seldom present, the number of types of ring structure is somewhat limited. The most common of the functional groups which are capable of forming rings of this type are

(1) $-COOH$ and $-NH_2$
(2) $-COOH$ and $=NOH$
(3) $-COOH$ and $-OH$
(4) $-COOH$ and $=S$
(5) $-CONH_2$ and $-NH_2$
(6) $-OH$ and $-OH$
(7) $-OH$ and $-NH_2$
(8) $-OH$ and $=NOH$
(9) $-OH$ and $=O$
(10) $-OH$ and $=N-$
(11) $=NOH$ and $=O$
(12) $=NOH$ and $=NOH$
(13) $=NOH$ and $=N-$

(14) $=NH$ and $=O$
(15) $=NH$ and $=NH$
(16) $=NH$ and $=N-$
(17) $-SO_3H$ and $-NH_2$
(18) $-SH$ and $=O$.

Chelate rings of type -C are obtained with molecules capable of forming two coordinate links. Rings containing two coordinate links are generally the least stable of the three types, since relatively stable molecules or ions are formed when the ring is broken. The most common examples of this type of structure are found in the complexes containing a powerful coordination centre such as cobalt, nickel, etc. Both 5-and 6-membered rings are known, but available evidence indicates that 5-membered rings form more easily. Rings of type -C containing more than 6-atoms either do not form or are extremely unstable. Rings containing 4 atoms are known. The functional groups involved in the formation of the rings of this type are:

(1) $-NH_2$ and $-NH_2$
(2) $-NH_2$ and $=N-$
(3) $-OH$ and $=NOH$
(4) $-NH_2$ and $=S$
(5) $-OH$ and $-OH$
(6) $=S$ and $=S$
(7) $=NOH$ and $=NOH$
(8) $=N-$ and $=N-$.

9(b). Chelate rings of class -3.

In systems of type-A, complexes are formed by the replacement of three hydrogen atoms of a tribasic acid by a metal atom. In $H_3Fe(PO_4)_2$ the phosphate radical apparently occupies three coordinating positions. (The situation, however, is very complicated).

In systems of type-B the following functional groups are involved in chelation

(1) two -OH and one -NH
(2) two -COOH and one -NH
(3) one -OH , one -COOH and one =N-
(4) one -OH , one =NOH and one =N-

The functional groups in the type-C are one -OH (acidic) and one -OH and one -NH- (donor).

The functional groups in type-D are three =N- .

9(c). Chelate rings of classes-4,5 and 6.

Few quadridentate, pentadentate and sexadentate groups are known, since the possibility of such coordination requires the fulfillment of specialised geometrical conditions in order that a strain-free structure may result.

The quadridentate systems of type-C involve the following functional groups:

(1) two -COOH and two -NH-
(2) two -OH and two =N-

(3) two -COOH and two =S

(4) two -NH- and two =N- .

The quadridentate systems of type-E contain the following characteristic groups:

(1) three $-NH_2$ and one -N-

(2) two $-NH_2$ and two -NH-

(3) four =N-

The sexadentate group prepared by Dwyer and Lions (17) contains two acidic (-OH) groups and four donor (two =N- and two =S) groups. All groups are appropriately disposed in space so as to enter the coordination sphere of a single central atom.

It should be pointed out that a given chelating agent would not always form the same polydentate structure. Thus a chelating agent which is capable of functioning as sexadentate with metals of coordination number 6, would necessarily be quadridentate with a tetracovalent metal. In the case of stable calcium complex with tetravalent anion of EDTA, it is not yet known whether calcium has a coordination number of 6 and the chelating agent is sexadentate (20) or calcium has a coordination number of 4 and the amino acid is quadridentate in character (21).

9(d). Functional groups and chelation.

The possibility of chelate formation arises wherever acidic and donor groups are suitably placed in the same molecule. It is a remarkable and quite unexplained phenomenon, however, that the presence of certain atomic groupings may confer the property of forming the chelate compounds more or less specifically with some particular metal, i.e. the chelate compound formed by that metal is characterised above all others by its stability and-as its usual corollary -its insolubility in water. The most familiar instance is the atomic grouping $-C(=NOH)--C(=NOH)-$, which is specific in this sense for nickel and palladium. Similarly, the atomic group specific for copper is $=C(OH)-\overset{|}{\underset{|}{C}}-C(=NOH)-$, and that for cobalt is $=C(OH)-C(-NO)=$.

10. <u>Ring size and chelation.</u>

While the chelate rings can be classified on the basis of the number of members contained in a ring, such a classification is necessarily arbitrary and more restricted than the broader one proposed above. Without doubt, the number of members in the ring plays a fundamental role in the formation of chelate rings and the ultimate solution of the subtle relations between the specificity of various organic compounds for certain metals and the structure of the molecule will rest on a consideration of the number of ring members and on their dimensions and mode of linkage.

For a molecule with two potentially coordinating groups to function as a chelate group, it must be geometrically possible to form a ring of low strain. Chelation will, therefore, be most favoured when the chelating groups are in 1:4 or 1:5 positions. When saturated rings are formed, 5-membered ring is the most stable. Objective proof of this has been furnished by Drew and Tress (22) who found that ethylene-diamine and less readily propylene-diamine coordinate with platinum whereas the higher diamines form only amorphous, ill-defined products, in which the two amino groups of any one molecule of diamine are probably linked to different metallic atoms. A particularly elegant demonstration of the superior stability of 5-membered ring as compared with 6-membered ring was given by Mann (23) in studying the coordination compounds of 1:2:3 triaminopropane. Further, Pfeiffer(24) has shown that, of $NH_2(CH_2)_n COOH$, those with n=1 or 2 alone function as chelating agents. When chelate rings involving double bonds are formed, the formation of 5- or 6- membered ring is favoured. The formation of larger ring, however, is not completely excluded; the 7- and 8-membered rings are considered to be present in the cobalt chelate complexes with succinato and sulphonyl diaceto radicals. (25;26).

11. Stability of the metal chelates.

During recent years, a number of workers have attempted to ascertain the factors that determine the stability of the coordinated complex and the way in which the stability changes with the change in the metal atom or the chelating group.

Pfeiffer, Thielert and Glaser (27) obtained some qualitative information from a study of the displacement of bivalent metal ion M_A^{++} from metal chelates with bis-salicylaldehyde ethylene-diamine by another bivalent metal ion M_B^{++} ; Pfeiffer concluded from these investigations that the sequence of stability of the metal chelates was

$$Cu > Ni > Fe > Zn > Mg \quad .$$

This order has been confirmed by more recent work.

A more quantitative approach to the problem emerges from a consideration of the successive equilibria involved in the formation of metal chelates. The method of deriving the required stability constants from the experimental data, in systems with stepwise equilibria, is not altogether straightforward, but the analysis of systems with successive equilibria and the method of evaluating the measurements have been worked out by J. Bjerrum (28) and have been applied by Calvin and Wilson (29), Mellor and Maley (30) and others in the study of the constitutive factors, depending on the particular metal and the structure of the complexing agent, which govern the formation of complex compounds.

Another quantitative approach to the problem has been based on the shift of the oxidation-reduction potentials accompanying complex formation. In the polarographic reduction, the oxidation-reduction potentials of successive stages in the process may be identified. Thus Calvin and Bailes (31) concluded from the studies of the polarographic reduction of the metal chelates of copper that of the two waves observed, the first wave represented the disruption of the complex as well as the transfer of one electron to the cupric ion. The results show very clearly that the structure of the chelating group affects the stability of the chelate compound in several ways: by modifying the electron-donor properties of the parent acid, by modifying the resonance in the double bond systems of chelating groups and -most frequently - by creation of rigid structures with appropriate stereochemical properties.

Whereas the shift in redox potential has afforded a clear measure of the influence of the structure of the chelating molecule, the potentiometric titration method provides a means of comparing the stability of compounds formed by any one complexing agent with various cations. It has emerged quite clearly from the studies of Mellor and Maley (32), Calvin and Melchior (33) and Irving and Williams (34) that, to a first approximation, the sequence of stability is the same, irrespective of the ligands involved:

$$\mathrm{Pd} > \mathrm{Cu} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Zn} > \mathrm{Cd} > \mathrm{Fe} > \mathrm{Mn} > \mathrm{Mg} \quad ,$$

a sequence with which Pfeiffer's earlier and qualitative results are in harmony.

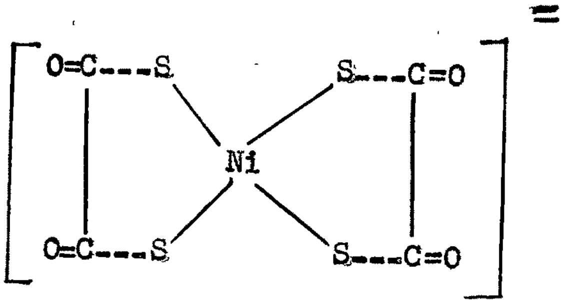
These results bear closely upon the specific function of the organic reagents in analytical chemistry. The formation of the metal chelates (non-electrolytes) involves the competition of the metal ions with hydrogen ion for combination with the anions. Hence the more stable the complex, the greater the concentration of the hydrogen ion at which it is capable of existing and the lower the pH value at which it can be precipitated or extracted from aqueous solutions.

12. Stereochemistry of 4-coordinate metal chelates.

For the spatial arrangement of four groups about a coordination centre, two possibilities come chiefly into question: a tetrahedral configuration or a square planar structure. Optical isomerism would be possible in the first case and geometrical isomerism in the second. Hence on chemical grounds, supported by physical evidence, it would be possible to arrive at the probable configuration.

12 (a). Stereochemistry of 4-covalent nickel.

It seems Pauling (35) was the first to suggest explicitly on theoretical grounds that nickel must be planar in the configuration of its 4-coordinate compounds. Before this, Tschugaeff (36) had already obtained two interconvertible compounds of nickel with methyl glyoxime. Sugden (37), shortly after Pauling's prediction, isolated two forms of the compound of nickel with benzyl methyl glyoxime, readily interconvertible, presumably related as cis and trans isomers. This assumption is supported by a considerable body of physical evidence. Cox, et al. (38) have shown by X-ray methods that the anion of the nickel compound



is rigidly coplanar and that the nickel salicylaldoximate has a trans planar structure. On the other hand, tetrahedral nickel chelates are considered to be formed in the case of bis-salicylaldehyde, bis-acetylacetonate, bis-ethylenediamine, etc.(39).

12 (b). Stereochemistry of 4-covalent palladium.

Palladium forms chelate compounds with dialkyl glyoximes, isomorphous with similar nickel chelates. Dwyer and Mellor (40) have obtained two forms of the compound of palladium with benzyl methyl glyoxime. Wardlaw, Sharratt and Pinkard (41) obtained cis and trans forms of diglycine palladium. This suggests a planar configuration for palladous complexes.

12 (c). Stereochemistry of 4-covalent platinum.

Although Werner (42), Grunberg (43) and Dickinson(44) suggested a planar configuration for platinous complexes, some workers maintained the possibility of tetrahedral arrangement of groups about platinum. Thus Reihlen (45) suggested a tetrahedral configuration for the platinous compound of ethylene bis-thioglycollic ether. Reihlen, et al. (46) and Rosenheim and Gerb (47) have claimed to have resolved the platinous chelate compounds; the optical activity, however, was very low. On the other hand, Drew (48), using unsymmetrical bifunctional chelating groups, found that the geometrical isomers of $[Pt(a-b)_2]X_2$ could be prepared. It is significant that both isomers were non-resolvable.

12 (d). Stereochemistry of 4-covalent copper.

Mills and Gotts (49) suggested a tetrahedral configuration for cupri-benzoyl pyruvic acid as its strychnine salt exhibited mutarotation. So much evidence is, however, available in favour of planar configuration for cupric complexes, that it seems assured that the conclusion reached by the above authors was in error and that copper is invariably planar in its 4-coordinate complexes. It has been shown from the study of the crystal structures that cupric complexes, such as salicylaldoximate, acetylacetonate, picolinate, etc. are planar (50). Stackelberg (51) has recently confirmed the planar configuration for a number of copper chelates of salicylaldehyde-imine type by means of X-ray crystal analysis. In no case, however, is geometrical isomerism known amongst complex and chelate compounds of copper.

It is noteworthy that the metals showing the greatest tendency for covalent bonding - Pt(II), Pd(II), Cu(II) and Ag(II) -

are very little affected by electronegativity differences in the donor group. Bivalent nickel, cobalt, iron and manganese ions are much more susceptible to differences in electronegativity of the donor group (52).

12 (e). Planar and tetrahedral structures.

The planar configuration thus appears to be normal for bivalent palladium, platinum and copper and is also found in the case of bivalent nickel, cobalt, silver, tin and lead. The configuration of most 4-coordinated elements, other than those indicated above is tetrahedral. This includes zinc, cadmium, mercury(53), beryllium (49; 54), etc. The evidence for the tetrahedral configuration of most of the elements is based upon the crystal structure of metal chelates or upon the optical resolution of bis-chelate compounds (55; 56). It seems, however, that under the constraint of groups of high coordinating power, the "planar" elements may be led to take up the other structure and vice versa (57; 58).

13. Chelation and magnetism.

The use of magnetic susceptibility measurements in the study of complexes arises from the fact that the electrons used in covalent bond formation are of necessity paired and so contribute nothing to the paramagnetic moment of the molecule. Paramagnetism is found mainly in the following classes of compounds (59):

(a) compounds of the transition elements (particularly the first series), owing to the presence of unpaired d-electrons;
(b) compounds of the rare earth and actinide series elements, owing to the presence of unpaired f-electrons;
(c) a few compounds of the first short period which contain unpaired p-electrons; and
(d) a few compounds which have no unpaired electrons.

Except in rare instances e.g. (d) above, paramagnetism arises from the presence of unpaired electrons in an atom. It is possible, therefore, to compute the number of paired and unpaired electrons in any complex. From a knowledge of the number of electrons used in covalent bond formation it is possible to deduce

(a) the nature of the orbitals involved and hence
(b) the valency, the bond type and the stereochemistry of the metal atom.

Magnetic measurements do not contribute much to our knowledge of the spatial configuration of 6-covalent (octahedral) complexes; but when the covalent structure leads to a square or to a tetrahedron, the information so obtained may be very valuable.

The ions of the first transition series starting with scandium and ending with zinc have progressively 0 to 10 electrons in 3 d shell. The first and last members are diamagnetic but all the others with intermediate numbers of electrons are paramagnetic. It might be supposed that these ions would be alternately paramagnetic and diamagnetic, depending on whether they have an odd or even number of electrons; but the ions are all paramagnetic because the electrons in the incomplete shell tend not to pair off until they are forced to do so. It is therefore easy to compute the number of unpaired electrons in any given metal complex.

Unpaired electrons have both spin angular momentum and orbital angular momentum. The difficulty arises in connection with the orbital contribution to the paramagnetic moment. Agreement with the experimental is, however, obtained by completely neglecting the orbital moment and calculating the magnetic moment according to the "spin-only" formula

$$\mu = \sqrt{n(n+2)}$$

where n is the number of unpaired electrons and μ is the magnetic moment expressed in Bohr magnetons.

The following table (60) gives a list of predicted magnetic moments for the ionic and covalent compounds of the transition metals. It shows where the magnetic criterion may be used to indicate bond type. Magnetic measurements should be of value in all cases where the susceptibility of the covalent structure differs from that of the ionic form. A distinction may be made between ionic and tetracovalent structures for Co(II), Ni(II), Pd(II), Pt(II) and Au(III);

other instances may be given, but these are the only metals commonly encountered in the transition group which form 4-covalent compounds involving d-orbitals.

transition series			predicted moment		
first	second	third	ionic	planar	octahedral
Sc(III),Ti(IV);	Y(III),Zr(IV); Nb(V),Mo(VI);	Hf(IV),Ta(V); W(VI);	0	0	0
V(IV);	Nb(IV),Mo(V);	W(V);	1.7	1.7	1.7
V(III),Cr(IV);	Mo(IV),Ru(VI);	W(IV),Re(V); Os(VI);	2.8	2.8	2.8
V(II),Cr(III); Mn(IV);	Mo(III);	Re(IV);	3.9	3.9	3.9
Cr(II),Mn(III); Fe(IV);	Mo(II),Ru(IV);	Os(IV);	4.9	4.9	2.8
Mn(II),Fe(III);	Ru(III);	Os(III),Ir(IV);	5.9	3.9	1.7
Fe(II),Co(III); Ni(IV);	Ru(II),Rh(III); Pd(IV);	Ir(III); Pt(IV);	4.9	2.8	0
Co(II);	Rh(II);	Ir(II);	3.9	1.7	
Ni(II);	Rh(I),Pd(II); Ag(III);	Pt(II); Au(III);	2.8	0	
Cu(II);	Ag(II);	-	1.7		
Cu(I);	Ag(I);	Au(I);	0		

14. Applications of chelation.

In the chelate compounds we have a field of widely different and important applications, a field which embraces almost all the applications of synthetic chemistry and stereochemistry with the possibilities of solving important problems in analytical chemistry and biochemistry. Some of the important applications are briefly considered here.

The chelate compounds have proved a very useful and fruitful tool in settling the questions related to the stereochemistry of the metals (61;62).

Complexes and chelates of metals have been extensively investigated for the analytical separation and estimation of metal ions by precipitation and for the estimation of metal ions by colorimetric methods (63;64;65;66). Besides, the metal ion separations can be effected by employing the new techniques of cation exchange and solvent extraction; chelate compounds are quite useful in connection with these methods (67;68). Further, the tendency of organic acids to form metal chelates explains the action of tartaric acid, citric acid, etc. in masking the reactions of heavy metals.

Schwarzenbach (69) has emphasised the usefulness of chelating agents as metal buffering agents in maintaining a nearly constant concentration of metal ion at almost any level of concentration. In order to accomplish this, a metal chelate is formed in presence of excess chelating agent.

The development of the theory of chelation provided a foundation for new developments in the field of colour lakes(70).

In biochemistry, chlorophyll, blood pigment and cytochrome are special (natural) chelates indispensable for life processes. The mechanism of the function of metals in the living organisms, is known to be chelate in nature.

In recent years a number of new amino-polycarboxylic acids which have the special property of forming water-soluble chelates have come into widespread use. These are used wherever the removal of useful ions is desirable, such as the softening of water, negative catalysis and clarification of solutions(71).

From the foregoing survey it will be readily understood that the chelate compounds have an unusual application to a variety of otherwise unrelated fields. It is a subject which offers abundant opportunities for exploration.

The aim of the present investigations was to study chelates and chelation through the application of the principle of chelation to the investigations on OXIMES. Hence a brief review of the chemistry of oximes will not be out of place.

15. Chemistry of oximes.

The term oxime was introduced by Victor Meyer (72) and implies the structure $>C=NOH$. Some members of this class are often described as isonitroso compounds, but there is no difference in structure or reactions between isonitroso compounds and oximes. The use of the term isonitroso tends to cause confusion; it is falling into disuse, its place being taken by the prefix oximino- (73). The term oxime used in the present discussion includes isonitroso group of compounds.

On reviewing the chemistry of oximes, it appears that the study of the oximes has been made from different aspects. It may be said that the investigations made in this field are in the following four different directions:

(1) investigations pertaining to the preparation of the oximino compounds;

(2) investigations (both chemical and physicochemical) regarding the properties and structures of the oximino compounds;

(3) investigations regarding the preparation, properties and structure of the metal chelates formed from the oximino compounds; and

(4) investigations pertaining to the utilisation of the oximino compounds in analytical chemistry and in other branches of science .

16. <u>Preparation of oximes</u>.

Victor Meyer and Zublin (72) first utilised hydroxylamine for the preparation of aldoximes and ketoximes from aldehydes and ketones respectively. The ease with which the reaction takes place varies widely with the aldehyde or ketone involved; in general, aldehydes react more easily than ketones and aliphatic ketones more readily than aromatic ones.

Victor Meyer (74) also obtained oximes by the action of nitrous acid on compounds containing reactive methylene group. It is now well established that nitrous acid is a reagent suitable for compounds containing reactive methylene group just as hydroxylamine is suitable for aldehydes and ketones.

Besides, (i) esters of nitrous acid in presence of suitable catalysts and (ii) nitrosyl chloride under specific conditions are also utilised in place of nitrous acid (75;76).

Other methods of preparing oximino compounds are

(1) oxidation of primary amine with Caro's acid (77),

(2) reduction of α-β-nitro olefin with zinc and acetic acid (78), and

(3) reduction of pseudonitrile with hydroxylamine (79).

17. Properties of oximes.

(1) Oximes possess acidic properties. They react with bases with the formation of salts.

(2) Oximes also possess basic properties. They react with acids with the formation of salts.

(3) Oximes are readily hydrolysed on boiling with dilute acids with the formation of aldehydes or ketones and hydroxylamine.

(4) Oximes can be smoothly acetylated. They can be alkylated yielding N-alkyl and O-alkyl ethers.

(5) They can be reduced by suitable reducing agents to primary amines. The reduction can be brought about by sodium and alcohol, sodium amalgam and acetic acid, or catalytically (80) by hydrogen in presence of nickel-keiselguhr.

(6) Action of dehydrating agents on the oximes: Aldoximes are dehydrated by acetyl chloride, etc. with the formation of nitriles. Ketoximes, on treatment with acetyl chloride, phosphorus pentachloride, etc., undergo a rearrangement reaction which is known as Beckmann transformation, usually with the formation of amides (81).

(7) Oximes can exist in various isomeric forms. The structural and stereo isomerism possible in oximes are discussed under the "structure of oximes".

(8) Oximes possess the property of reacting with the transitional metals and this property is usually specific of the metals and of the oximes.

(9) Viscosities of aromatic aldoximes have been determined(82) and are found to be exactly parallel with those of the corresponding acids.

(10) Dielectric constants and dipole moments of the oximes and of their methyl ethers have been determined and correlated with their structures(83;84).

(11) Some of the monoximes and dioximes have been investigated for their ultraviolet absorption (85;86) and are found to have continuous absorption in the ultraviolet region (220 to 300 mμ).

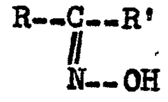
(12) Infra red spectra of some glyoximes have been determined (87) and the bands are interpreted as follows:

Group	Band
-OH	320 and 760 cm.$^{-1}$
=NO	1150 cm.$^{-1}$
C=N	1625 cm.$^{-1}$

(13) Raman spectra of some oximes have been investigated (88; 89;90) and the Raman frequency for C=N is found to be 1630 and 1660 cm.$^{-1}$.

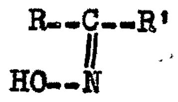
18. Structure of oximes.

In the last decade of the last century, the question about the structure and isomerism of oximes was tackled by a number of investigators. Goldschmidt (91) observed that benzildioxime could be converted into isomeric compound by heating its alcoholic solution. Beckmann (92) also showed that benzaldioxime exists in two isomeric forms. The first remarkable interpretation of this isomerism was made by Hantzsch and Werner (93) in 1890, who proposed a method of assigning structures to aldoximes and ketoximes. They pointed out that if three valencies of nitrogen atom in the oxime do not lie in the same plane, there should be an analogy between the isomerism of oximes and that (i.e. cis-trans isomerism) in the olefin series. The isomers would be



$R{-}\underset{\underset{N{-}OH}{\|}}{C}{-}R'$

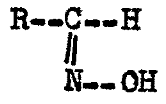
(a)



$R{-}\underset{\underset{HO{-}N}{\|}}{C}{-}R'$

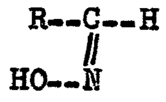
(b)

for ketoximes and



$R{-}\underset{\underset{N{-}OH}{\|}}{C}{-}H$

(a)



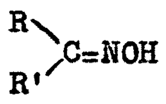
$R{-}\underset{\underset{HO{-}N}{\|}}{C}{-}H$

(b)

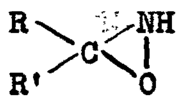
for aldoximes.

Hantzsch' method of orienting aldoximes depended on the fact that an acetyl derivative of one isomer regenerated a parent oxime on treatment with an alkali, whilst an acetyl derivative of the other lost acetic acid producing a nitrile. He assumed that the elimination of acetic acid took place from cis and not from the trans isomer. Similarly, a structure to the ketoximes was ascribed on the basis of Beckmann rearrangement wherein cis-interchange of radicals was assumed to take place.

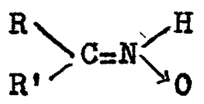
In 1921, Atack and Whinyates (94) reported the discovery of another isomer of benzildioxime and partly on the strength of this, they levelled a strong critism against Hantzsch and Werner's theory and put forth a purely structural theory. They postulated such structural isomers as



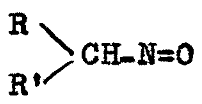
(oxime)
(a)



(isoxime)
(b)



(nitrone)
(c)



(nitroso)
(d)

The isomers (b) and (d) contain asymmetric carbon atom and hence should be resolvable; however, no oximes have been obtained in which optical activity is due to oxime grouping. The nitrone structure (c) has received considerable attention. Actually, the alkylation of a symmetrical oxime produces two isomeric products -one O-alkylated and the other N-alkylated (95). It proves the existence of isomers (a) and (c) and provides a strong evidence in favour of Atack's theory.

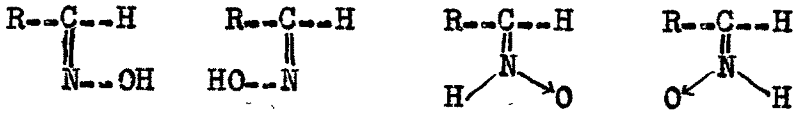
Brady and coworkers (96;97) have, however, reported two isomeric O-ethers. This is an evidence in favour of Hantzsch' theory. Thus both structural and stereochemical theories are necessary to account for the isomerism of the oximes.

It was suggested by Bucherer (98) in 1914 and shown experimentally by Meisenheimer (99) in 1921 that Beckmann rearrangement took place by trans-interchange of radicals. Various observations, made thenafter, confirmed this conclusion (81;100). This required a change in the configurations previously assigned to ketoximes.

Similarly, it was put forth by Beckmann (101) and shown by Brady (97) that the elimination of acetic acid from an acetyl derivative of aldoximes was a trans effect. This led to configurations opposite to those assigned to aldoximes earlier.

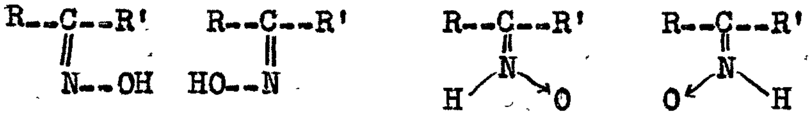
Thus chemical and stereochemical evidence leads to the following configurations for the monoximes:

(i) for aldoximes



(a) (b) (c) (d)

(ii) for ketoximes



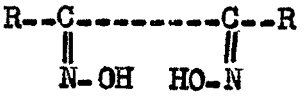
(a) (b) (c) (d)

Taylor and Ewbank (102), from the study of the volatility, solubility and the carbonyl reactivity of the isomeric monoximes of a-β-diketones, conceived that the existance of hydrogen-bond can explain the physical and chemical differences of these compounds.

Sutton and Taylor (83) studied the isomerism of the oximes by determining the dipole moments of the isomeric oximes and found appreciable difference in the values of dipole moment of α-and β-isomers of N-methyl ethers of p-nitrobenzophenone oxime. Parsons and Porter (103), however, observed that in the case of o-, m- and p-chloro benzophenone oximes, the results of dipole moment investigations did not give an unambiguous answer to the question of oxime structure.

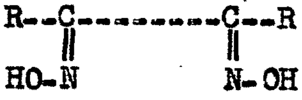
Palm and Werbin (104) have shown that the OH stretching frequencies of α-and β-isomers of oximes are different and can be used for distinguishing between them.

In the case of symmetrical dioximes three geometrical isomers can exist, thus



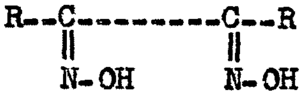
$$\underset{\text{N-OH}}{\overset{\text{R--C}}{\|}}\text{--------}\underset{\text{HO-N}}{\overset{\text{C--R}}{\|}}$$

syn



$$\underset{\text{HO-N}}{\overset{\text{R--C}}{\|}}\text{--------}\underset{\text{N-OH}}{\overset{\text{C--R}}{\|}}$$

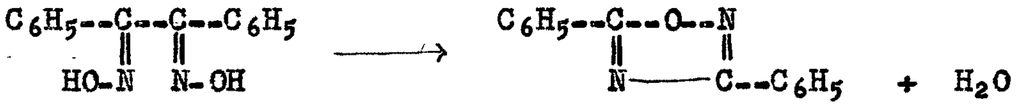
anti



$$\underset{\text{N-OH}}{\overset{\text{R--C}}{\|}}\text{--------}\underset{\text{N-OH}}{\overset{\text{C--R}}{\|}}$$

amphi

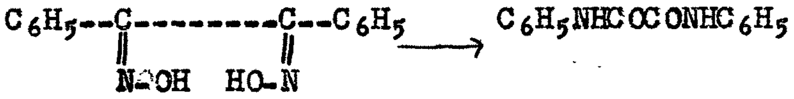
Three benzildioximes, namely α, β and γ, were obtained and investigated by Meisenheimer (105;106). It was observed that on Beckmann rearrangement, α-dioxime furnished azoxine, β-dioxime, oxanilide and γ-dioxime, benzoyl phenyl urea. On the assumption that a trans shift is involved in the rearrangement, α-dioxime should have an anti-configuration.



$$C_6H_5\text{--}\underset{\text{HO-N}}{\overset{C}{\|}}\text{--}\underset{\text{N-OH}}{\overset{C}{\|}}\text{--}C_6H_5 \longrightarrow C_6H_5\text{--C--O--N}, \ \text{N}\text{---}\text{C--}C_6H_5 + H_2O$$

,

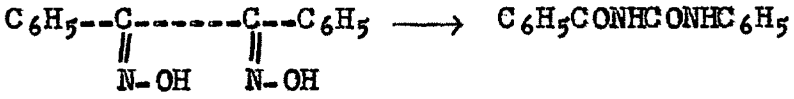
and β-dioxime a syn-configuration



$$C_6H_5\text{--}\underset{\text{N-OH}}{\overset{C}{\|}}\text{--------}\underset{\text{HO-N}}{\overset{C}{\|}}\text{--}C_6H_5 \longrightarrow C_6H_5NHCOCONHC_6H_5$$

.

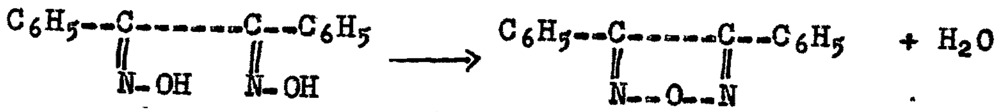
Amphi configuration can be suggested on the basis of either cis or trans shift of radicals on rearrangement.



$$C_6H_5\text{--}\underset{\text{N-OH}}{\overset{C}{\|}}\text{------}\underset{\text{N-OH}}{\overset{C}{\|}}\text{--}C_6H_5 \longrightarrow C_6H_5CONHCONHC_6H_5$$

.

Further evidence added in confirmation of amphi-configuration of γ-dioximes was that it could be converted into a cyclic compound on dehydration.



$$\underset{\substack{\| \\ N-OH}}{C_6H_5-C}-\underset{\substack{\| \\ N-OH}}{C}-C_6H_5 \longrightarrow \underset{\substack{\| \\ N-O-}}{C_6H_5-C}-\underset{\substack{\| \\ N}}{C}-C_6H_5 + H_2O$$

The differences in the ability of isomeric dioximes to form complex compounds with metal ions are discussed under "metal chelates of dioximes."

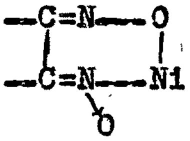
19. Metal chelates of dioximes.

In 1905 the Russian chemist Tschugaeff (6) first prepared the metal chelate of bivalent nickel with dimethyl glyoxime. Feigl (107) in 1924 studied the formation of tetravalent nickel complex with the same reagent. Tschugaeff (108) also prepared and studied the complexes of rhodium with dimethyl glyoxime and those of iron, cobalt and palladium with dimethyl glyoxime and ammonia, pyridine, etc. Kubina and Plicta (109) studied the action of bismuth salts on dimethyl glyoxime and ammonia. Sugden (37) and Dwyer and Mellor (40) obtained the isomers of nickel and palladium complexes of benzyl methyl glyoxime.

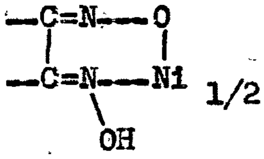
Other dioximes, investigated for their reaction with nickel, are (i) α-benzildioxime (110), (ii) γ-benzildioxime (111), (iii) oxalene diamidoxime (112), (iv) oxalene diuramidoxime (113), (v) alicyclic dione dioximes (114;115), etc.

19. (a) Structure of nickel and palladium chelates with dioximes.

Of the three isomers of vicinal dioximes, β-dioximes are incapable of forming metallic complexes, γ-dioximes form yellow or greenish yellow compounds with nickel in which only one molecule of the dioxime is attached to one atom of nickel, and α-dioximes form red or reddish yellow nickel complexes in which two molecules of the dioxime are attached to one atom of nickel. The compound formed by the γ-dioxime with nickel may be represented as

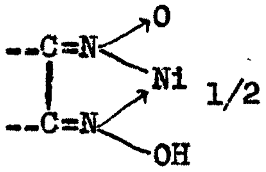


Similarly, the compound formed by α-dioximes with nickel was regarded by Tschugaeff (6) as a six-membered ring of the following composition.



on the assumption that the α-dioxime was a syn-isomer. According to Meisenheimer's interpretation of Beckmann rearrangement, however, α-dioxime should be regarded as an anti-isomer.

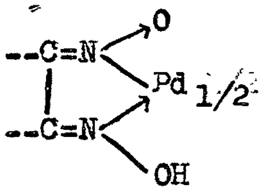
It was at first difficult to understand how a six-membered ring could be formed from an anti-dioxime in which the OH groups are directed away from one another. This was understood, however, with the knowledge of the fact that the oxime group exists in two tautomeric forms (95). By assuming the tautomeric nitrone group to be involved in the formation of the nickel derivative, a five-membered ring is formed in which the nickel atom is attached directly to nitrogen atom



Pfeiffer (116;117), who first suggested this formula, offered as evidence for this structure the fact that metal-nitrogen linkage is quite common among coordination compounds, and that the colours of the very similar compounds are practically identical.

OH group of the second oxime group is not involved in the formation of the metal complex. This is demonstrated by the fact that the mono O-methyl ethers of the dioxime form exactly similar compounds with nickel (116). Pfeiffer (116) also showed that when one of the oxime groups is replaced by an imino or methyl imino group, the resulting compounds form complexes in the same manner as α-dioximes.

Tschugaeff (108) and Wunder and Thuringer (118) have prepared the complex of palladium with dimethyl glyoxime and have shown that its formula is analogous to that of nickel dimethyl glyoxime. Hence it can be represented as shown on the next page.



Sugden (37) and Dwyer and Mellor (40) isolated and identified geometric isomers corresponding to the cis- and trans- configurations of the nickel and palladium derivatives of several unsymmetrically substituted α-dioximes. This evidence for the planar structure of these molecules has been confirmed by magnetic measurements (119;120;121;122). The metal chelates have been found to be diamagnetic indicating the square planar structure with dsp^2 bonds. Further proof for the structure of these chelate compounds has been established by means of X-ray analysis (123;124;125).

It has long been assumed (126) that hydrogen bonding occurs between the remaining oxime hydrogens and the proximate oxygens of the nitrone-form oxime groups. Chemical evidence indicating a lack of reactivity or at least greatly decreased reactivity of these hydrogens has been provided by Tschugaeff (126), Barker (127) and Brady and Muers (128). Nature of the hydrogen bond in some nickel dioximates has been investigated recently (129).

20. Oximes as analytical reagents.

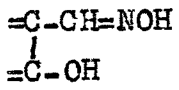
Many oximes have been found to possess valuable analytical properties. These compounds form "salts" either by replacement of the hydrogen atom of the oxime group or by the coordinating properties of the oxime nitrogen atom. Many of these "salts" are insoluble and usually coloured, which make them important in analytical procedures. Most of the analytically important oximes belong to either of the two classes (a) monoximes and (b) dioximes.

20 (a). Monoximes.

Analytically important monoximes may be classified as (i) acyloin oximes, (ii) ortho-hydroxy aromatic oximes, (iii) ketone oximes, (iv) nitroso phenols and (v) miscellaneous oximes.

(i) α-acyloin oximes react with cupric salts to form green, water-insoluble complexes. In these compounds, α-acyloin oximes appear to have functioned as dibasic acid (130). Under special conditions α-benzoin oxime forms compounds with cobalt, nickel, etc., but in the formation of these substances, the oxime functions as a monobasic acid (131). It is also used for the quantitative precipitation of molybdenum (132) and tungsten (133); the insoluble compounds in the two cases appear to be the addition products of molybdic or tungstic acid with the oxime.

(ii) Ortho-hydroxy aromatic oximes e.g. salicylaldoxime containing the group =C-CH=NOH / =C-OH form light yellowish to greenish copper "salts" which are insoluble in dilute acetic acid (134; 135). Salicylaldoxime is also found useful for the determination of lead (136),



$$\begin{array}{l}=C-CH=NOH\\ \;\;|\\ =C-OH\end{array}$$

palldium(137),iron(138),nickel(139),bismuth(140) and vanadium(140).

(iii) Ketone oximes:The group $\begin{array}{l}-\mathrm{C}=\mathrm{O}\\ \;|\\ -\mathrm{C}=\mathrm{NOH}\end{array}$, in open aliphatic chains,is analytically important since it confers upon the molecule the property of inner complex formation. One of the most interesting reactions of compounds of this type is the so-called "iron-blue" reaction,which was first observed by Whiteley (141).Feigl and co-workers (142) have investigated the relationship between structure and the reaction.

(iv) Nitroso phenols: A number of analytically important compounds containing the grouping $\begin{array}{l}=\mathrm{C}-\mathrm{OH}\\ \;\;|\\ =\mathrm{C}-\mathrm{NO}\end{array}$ are known in which the two carbon atoms are a part of a ring structure.Best known of these are α-nitroso β-naphthol, β-nitroso α-naphthol and o-nitroso phenol,which react specifically with cobalt (143).They are considered to react in their tautomeric quinone - oxime form.

(v) Miscellaneous oximes: A number of aldoximes and ketoximes such as formaldoxime,acetaldoxime,benzaldoxime,acetoneoxime, etc. have been investigated as reagents for cobalt,nickel, copper,etc (144;145;146;147).

20 (b). Dioximes.

In 1905,Tschugaeff(108)first discovered the reaction between nickel salts and dimethyl glyoxime which yields brilliant red, insoluble nickel chelate. The insolubility of this compound has made possible the use of dimethyl glyoxime as analytical reagent for the detection and estimation of nickel. Various other dioximes have also been investigated and found useful as analytical reagents. Brunck (148), in a series of investigations applied the Tschugaeff reaction to the separation and gravimetric estimation of nickel. Since then, a large number of papers have appeared, confirming and extending the work of Brunck. Feigl (107) has described a test involving the formation of tetravalent nickel complex of dimethyl glyoxime. He claims that this reaction is about four times as sensitive as Tschugaeff reaction.

The reaction of dimethyl glyoxime with palladium was first observed by Tschugaeff (108) and was later used by Wunder and Thuringer (118) for the separation and estimation of palladium.

Braley and Hobart (149) used the reaction between cobalt and dimethyl glyoxime for the detection and estimation of cobalt.

Although Tschugaeff (108) observed that ferrous iron reacts with ortho-dioximes in the presence of ammonia, pyridine, etc., to form soluble red or violet compounds, Slawik (150) was the first to apply this reaction as an extremely sensitive test for iron.

Certain oxidising agents when added to the alkaline solutions of cupric salts containing dimethyl glyoxime,produce an intense reddish violet colour. This reaction was first observed by Clarke and Jones (151) and was later studied and applied as an analytical reaction by Hurd and Chambers(152), Kolthoff (153) and Goethals (154).

Kubina and Plicta (109) observed that when a solution of the chloride or nitrate of bismuth is treated with dimethyl glyoxime and the hot solution is then made strongly alkaline with ammonia,an intense yellow voluminous precipitate is formed.

The use of dimethyl glyoxime to detect vanadium, cerium and tin indirectly has been suggested by Ephraim(155), Beck(156) and Feigl (157) respectively.

The other dioximes investigated as analytical reagents are (i) α-benzildioxime for nickel(158;159),(ii)α-furyl dioxime (160;161) for nickel and platinum-group metals, (iii)benzoyl methyl glyoxime for palladium (162;163;164), (iv) oxalenediamidoxime for nickel and palladium(112;165), (v) oxalenediuremidoxime for nickel (113;162;166) and (vi) alicyclic dione dioximes for nickel and palladium(115; 167;168;169;170).

21. Aim of present investigations.

From the above studies it was considered that if α-oximino derivatives of the substituted amides of acetoacetic acid were prepared and converted into α-β-dioximes, these compounds would prove useful in the investigations on the different aspects of oxime chemistry.

Our present knowledge about the oximes of aceto-acetic acid and its derivatives is as follows:

Victor Meyer (73) prepared α-oximino derivative of ethyl aceto-acetate by the action of nitrous acid(Sodiun nitrite and hydrochloric acid). The same was also obtained by the action of sodium nitrite and acetic acid(171), by the action of amyl nitrite in ether solution(172) and by the action of nitrosyl chloride in benzene solution(141) on the ester.

Knorr(173) prepared the α-oximino derivative of acetoacetanilide by the action of nitrous acid, while Naik, Trivedi and Mankad (174)obtained the α-oximino derivatives of acetoacet(aryl)amides (where aryl = phenyl, o-tolyl, p-tolyl, 3:4-xylyl, α-naphthyl or β-naphthyl)by the action of nitrosyl chloride in benzene solution.

α-oximino acetoacetic ester(ethyl), on reduction with aluminium amalgum yielded a pyrazine derivative(175). The reduction was also carried out with Raney nickel and hydrogen by Adkins and Reeve (171) and with tin and hydrochloric acid by Gabriel and Posner (176).

The absorption spectra of α-oximino acetoacet(aryl) amides in the ultraviolet region were investigated by Naik, Trivedi and Mankad (177).

Taylor and Ewbank (178) observed that α-oximino derivative of ethyl acetoacetate formed complexes with copper, nickel and cobalt.

Schiff (179;180) prepared β-oximes of ethyl acetoacetate, aceto-acetanilide and α-chloro-aceto-acetanilide. Knorr and Reuter (181) prepared β-oximino and α-β-dioximino acetoacetanilide, while Rodionov et al. (182) prepared α-oxime and α-β-dioxime of ethylacetoacetate. Khromov(183) prepared β-oxime of acetoacetic acid.

β-oximino derivatives spontaneously decomposed into isoxazolone derivatives (184;185;186).

It appeared from these studies that some of these oximes would exhibit internal chelation and that the principle of chelation would be applicable to these investigations.

With this view, it was proposed

(1) to prepare α-oximino and α-β-dioximino derivatives of some aryl amides of acetoacetic acid,

(2) to prepare the metal chelates of these oximino compounds using the salts of some transitional elements,

(3) to determine the magnetic susceptibility of some of the metal chelates prepared,

(4) to investigate the absorption spectra of these oximes and some of their metal chelates,

(5) to study the stereochemistry of these oximes and their metal chelates from the data obtained and

(6) to investigate the applicability of these oximes as analytical reagents in the detection and the estimation of the metals.

For the purpose of these investigations the following amides of acetoacetic acid were taken as the starting materials:

(1) acetoacetanilide
(2) acetoacet-o-toluidide
(3) acetoacet-o-chloranilide
(4) acetoacet-o-anisidide
(5) acetoacet-p-chloranilide
(6) acetoacet-p-phenetidide
(7) acetoacet-2:4-xylidide

The investigations carried out with these substances, with the above considerations in view, and the discussions of the results obtained are presented in the following pages.