INTRODUCTION

INTRODUCTION

I.1 General :-

Modern technological demands for materials which have desirable mechanical thermal and/or electrical characteristics at increasingly higher temperatures as well as at the low and ambient temperatures have directed the attention of investigators to polymeric systems which may be strictly inorganic or inorganic-organic in character. Inorganic-organic polymers consist mainly of polymers concontaining (a) Si, P, B, etc. (b) C-bonded metals and metalloids and (c) Co-ordinated or chelated metals. They are tabulated with references as folows : (tables are not exhaustive) :

(a) Polymers containing Si (including Polysiloxanes and poly metallosiloxanes)	..... Table 1
(b) Polymers containing P	..... Table 2
(c) Polymers containing B	..... Table 3
(d) Organometallic Polymers	..... Table 4
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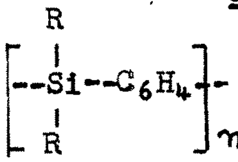
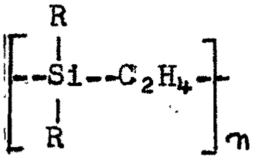
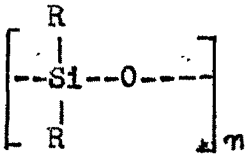
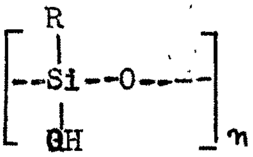
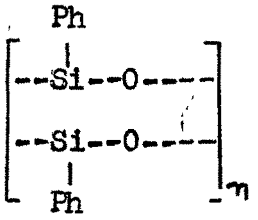
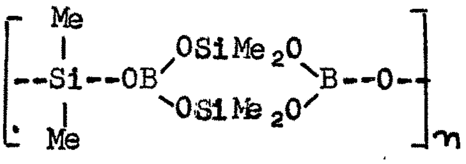
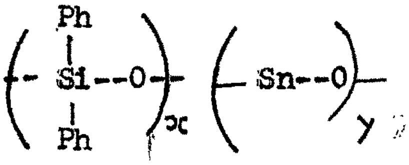
(i) from O-ligands	..... Table 5
(ii) from O,N-ligands	..... Table 6
(iii) from N-ligands	..... Table 7
(iv) from N-S ligands	..... Table 8
(v) from Polymeric ligands	..... Table 9
(vi) from Co-ordination complexes	..... Table 10

Table - 1

Polymer Containing Si

No.	Compound	Reference
1.	 $\left[\text{--}\overset{R}{\underset{R}{\mathrm{Si}}}\text{--}C_6H_4\text{--}\right]_n$	1
2.	 $\left[\text{--}\overset{R}{\underset{R}{\mathrm{Si}}}\text{--}C_2H_4\text{--}\right]_n$	2
3.	 $\left[\text{--}\overset{R}{\underset{R}{\mathrm{Si}}}\text{--}O\text{----}\right]_n$	3,4,5,6
4.	 $\left[\text{--}\overset{R}{\underset{OH}{\mathrm{Si}}}\text{--}O\text{----}\right]_n$	7
5.	 $\left[\begin{array}{l}\text{--}\overset{Ph}{\mathrm{Si}}\text{--}O\text{----}\\ \text{--}\underset{Ph}{\mathrm{Si}}\text{--}O\text{----}\end{array}\right]_n$	8
6.		9
7.	 $\left(\text{--}\overset{Ph}{\underset{Ph}{\mathrm{Si}}}\text{--}O\text{--}\right)_x\left(\text{--}Sn\text{--}O\text{--}\right)_y$	10

(Contd.)

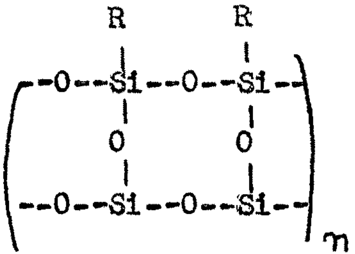
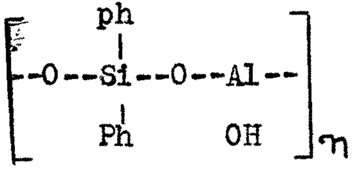
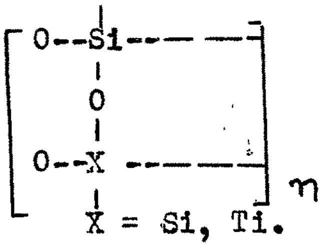
No.	Compound	References
8.		11
9.		12
10.	 X = Si, Ti.	13

Table - 2.

Polymers containing P

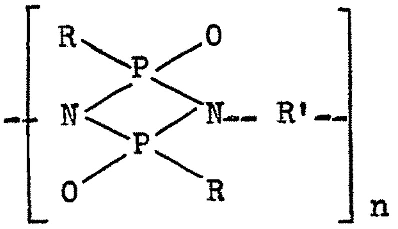
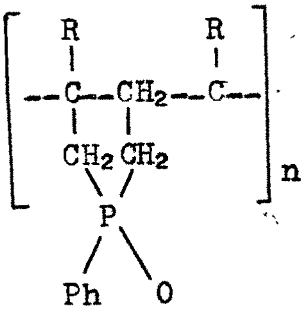
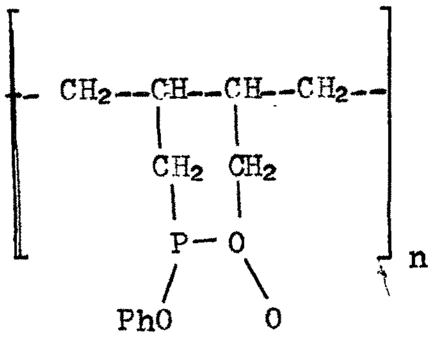
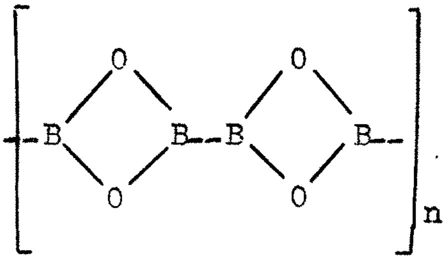
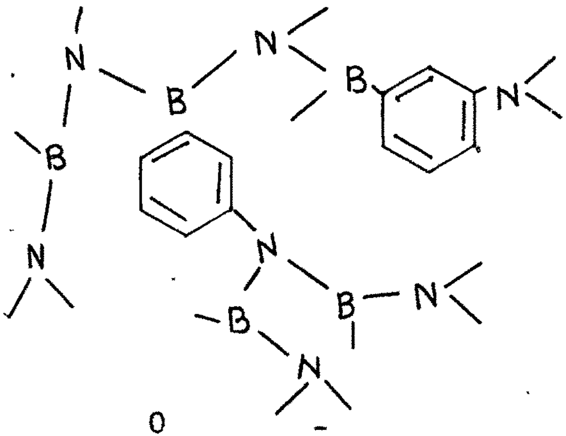
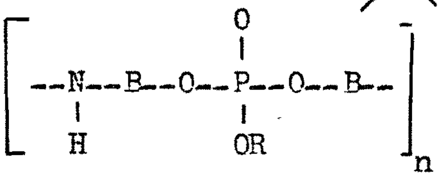
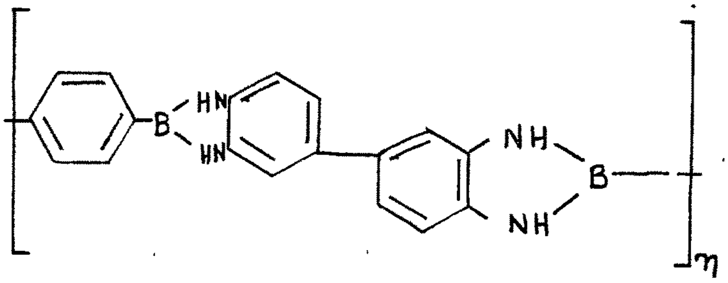
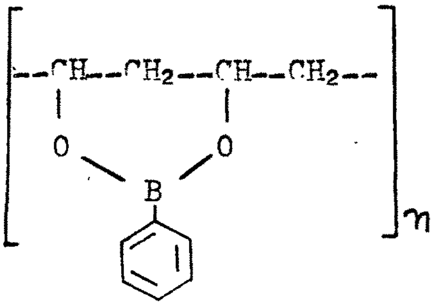
No.	Compound	References
1	$\left[NP(CF_3)_2\right]_n$	14
2	$\left[NP(OCH_2CF_3)_2\right]_n$	15
3		16
4	$(RPO_2)_n$	17
5		18
6		18

Table - 3

Polymers containing B

No.	Compound	References
1		19
2		20
3	 $\left[-\underset{H}{N}-B-O-\overset{O}{\underset{OR}{P}}-O-B- \right]_n$	21
4		22
5		23

(Contd.)

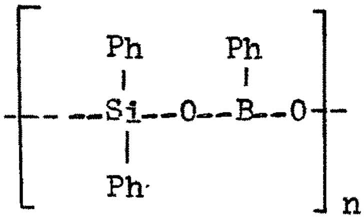
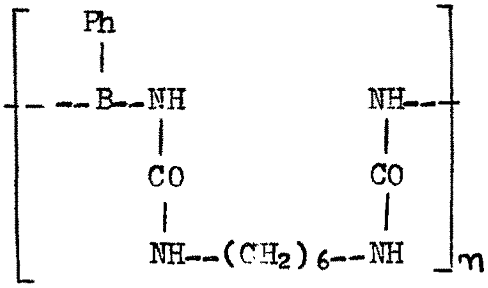
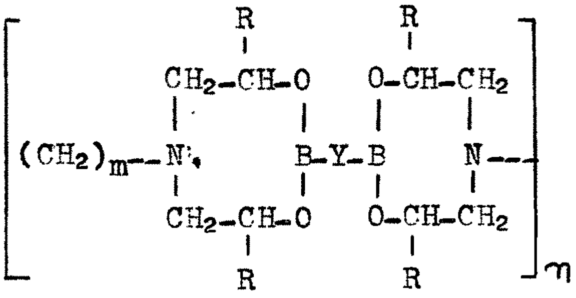
No.	Compound	References
6	 $[-Si(Ph)_2-O-B(Ph)-O-]_n$	24
7	 $[-B(Ph)-NH-CO-NH-(CH_2)_6-NH-CO-NH-]_n$	25
8		19

Table - 4.

Organometallic polymers.

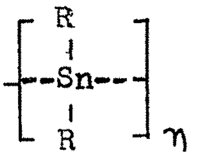
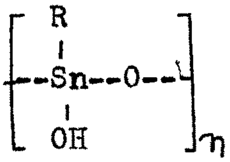
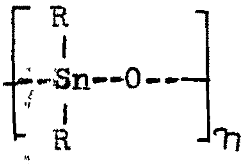
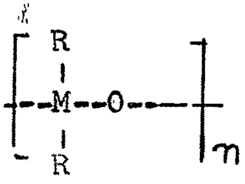
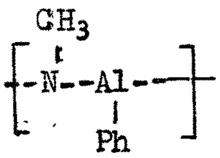
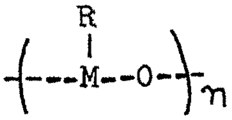
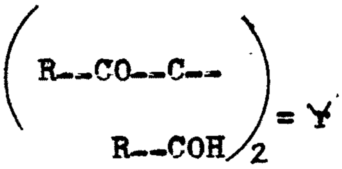
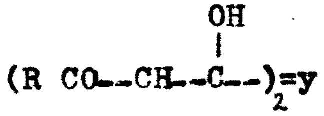
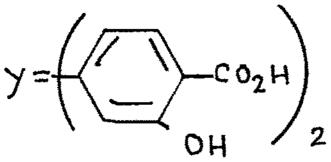
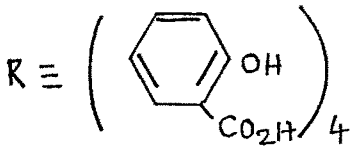
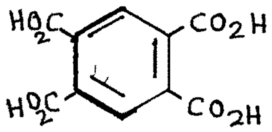
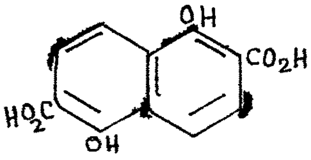
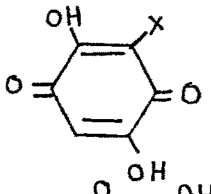
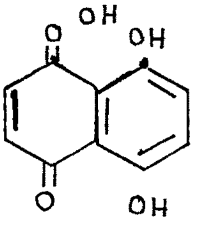
No.	Compound	References
1.	 $\left[-\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{Sn}}}-\right]_n$	26,27
2.	 $\left[-\overset{\mathrm{R}}{\underset{\mathrm{OH}}{\mathrm{Sn}}}-\mathrm{O}-\right]_n$	28
3.	 $\left[-\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{Sn}}}-\mathrm{O}-\right]_n$	29
4.	 $\left[-\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{M}}}-\mathrm{O}-\right]_n$ (M = Ti, Sn)	30
5.	$(\mathrm{R_2SnS})_n$	31
6.	 $\left[-\overset{\mathrm{CH_3}}{\mathrm{N}}-\underset{\mathrm{Ph}}{\mathrm{Al}}-\right]$	32
7.	 $\left(-\overset{\mathrm{R}}{\mathrm{M}}-\mathrm{O}-\right)_n$ (M = Al, B)	30

Table - 5

Co-ordination polymers from O-ligands

No.	Ligand	Metalions	Referendes
1	 $\left(\begin{array}{l}R{-}{-}CO{-}{-}C{-}{-}\\ \quad R{-}{-}COH\end{array}\right)_2 = Y$	Cu, Ni, Co, Zn, Cd, Hg, Be, Mg, Mn, Al.	33 to 46
2	 $(R\ CO{-}{-}CH{-}{-}\overset{\overset{OH}{\vert}}{C}{-}{-})_2{=}y$	Cu, Ni, Co, Fe	47 to 49
3		Cu, Zn	50, 51
4		Cu, Fe, Be, Ag, Al, Mg.	52
5		Th, U.	53
6		Zn, Ni, Fe.	53
7		Cu, Ni, Cd.	54 to 60
8		Cu, Ni, Co, Zn, Be	60 to 63

(Contd.)

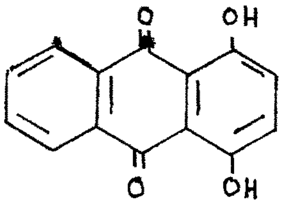
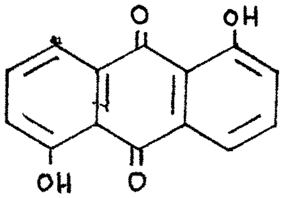
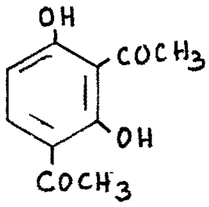
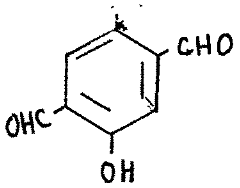
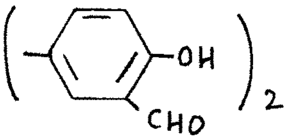
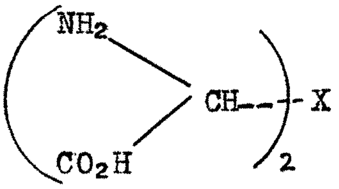
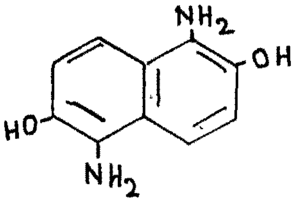
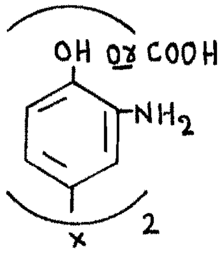
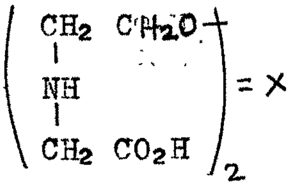
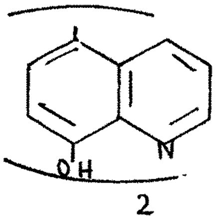
No.	Ligand	Metalions	References
9		Zn,Cu,Ni,Co,Mn, Cd.	60 to 71
10		Zn,Cu,Ni,Co,Fe, Pb,Sn.	65 to 71
11		Zn,Cu,Ni,Co,Fe, Pb.	71
12		Co	62
13	Y = 	Cu,Ni	72 to 74

Table - 6

Co-ordination polymers from O, N ligands.

No.	Ligand	Metalions	References
1	$(CH_3\ CO\ CH_2\ CO)C_6H_4\ NHCH_2-CO_2H$	Zn,Co,Ni,Be, Mg,Pb,Uo_2	75
2	 C	Cu,Co	76
3		Co	60
4		Cu	76, 77
5	 $\left(\begin{array}{ll} CH_2 & CH_2O- \\ \mid & \\ NH & \\ \mid & \\ CH_2 & CO_2H \end{array}\right)_2 = X$	Ni,Cu.	78
6		Cu,Ni,Co,Mn, Zn,Cd.	77 to 84

(Contd.)

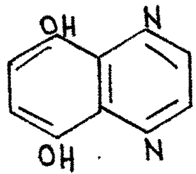
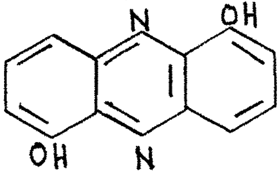
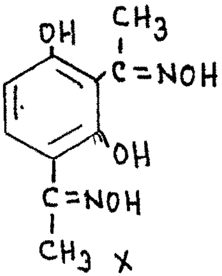
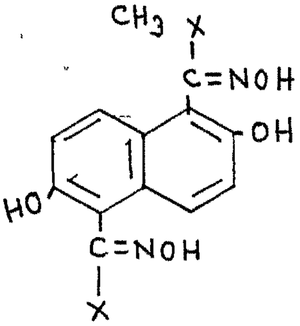
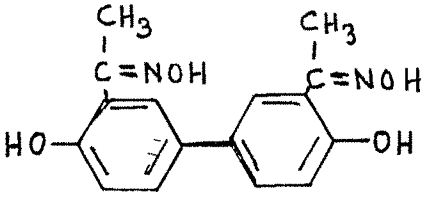
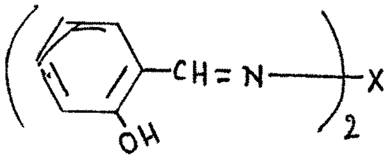
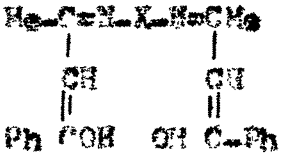
No.	Ligand	Metal ions	References
7		Cu,Ni,Co	60
8		Cu,Ni,Cd	54, 55
9		Zn,Cu,Ni,Co, Fe,Pb,Sn.	71
10		Cu,Ni,Pd	60, 85.
11		Cu	96
12		Cu,Ni,Co	72 to 74
13	 $\begin{array}{ccccc} Me- & C & =N-X-N= & C & -Me \\ & \vert & & \vert & \\ & CH & & CH & \\ & \Vert & & \Vert & \\ Ph & COH & & OH\ C & -Ph \end{array}$	Cu	97

Table - 7

Co-ordination polymers from N-ligands

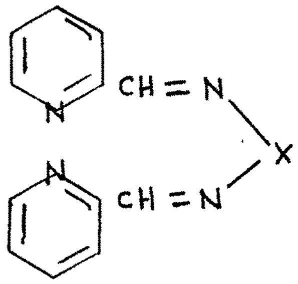
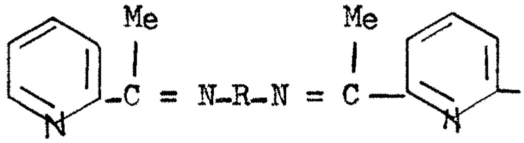
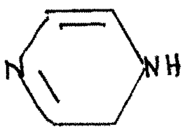
No.	Ligand	Metalions	References
1			88
2		Co,Ni,Fe.	89
3		Zn,Cu,Co.	90

Table - 8

Co-ordination polymers from N, S ligands

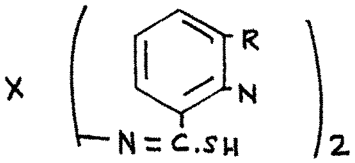
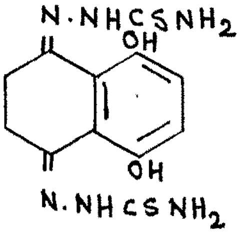
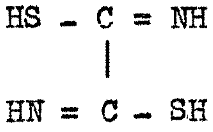
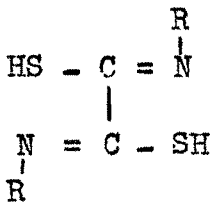
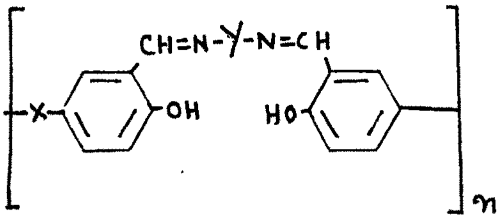
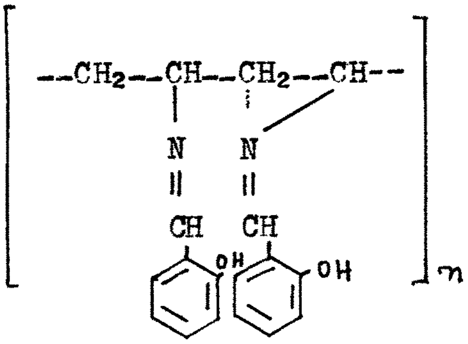
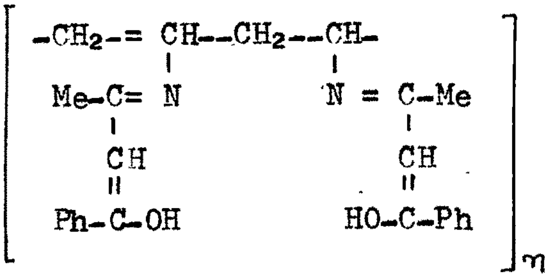
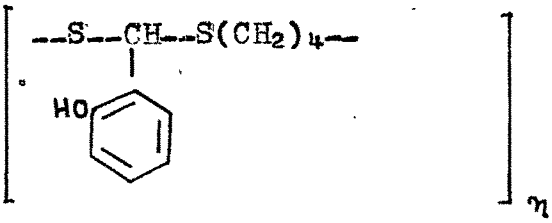
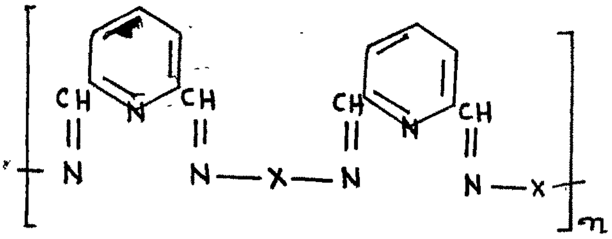
No.	Ligand	Metalions	References
1		Cu,Ni,Zn,Co	91 to 94
2		Zn,Ni	95
3	 $\begin{array}{ccccc} HS & - & C & = & NH \\ & & \vert & & \\ HN & = & C & - & SH \end{array}$	Cu,Ni,Co.	55, 96 to 98
4	 $\begin{array}{ccccc} & & & & R \\ & & & & \vert \\ HS & - & C & = & N \\ & & \vert & & \\ N & = & C & - & SH \\ \vert & & & & \\ R & & & & \end{array}$	Cu,Ni	99

Table - 9

Co-ordination polymers from polymeric ligands

No.	Ligand	Metal ions	References
1		Cu,Ni,Co,Zn, Cd,Fe,Al,Cr	100 to 104
2		Zn,Cu,Ni,Co, Fe	105
3		Cu,Ni,Co,Zn, Fe.	106
4		Zn,Cu,Ni.	107
5		Cu,Fe.	108

(Contd.)

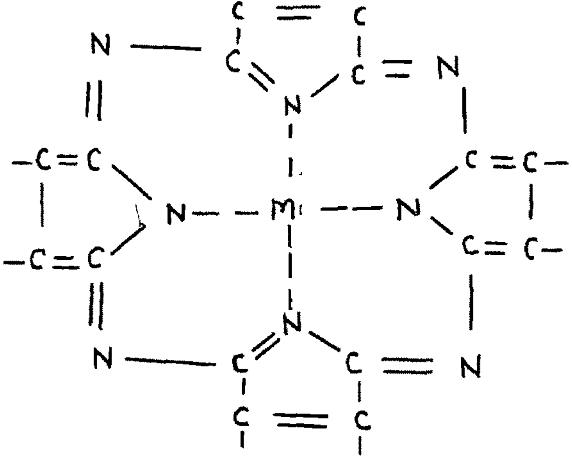
No.	Ligand	Metalions	References
6		Cu.	109 to 112
7	Polyoximes		113

Table 2-10

Coordination polymers from coordination complexes

No.	Coordination complex	Polymerization	References
1	Veinyl ferrocene	Veinyl polymerization Diene polymerization	114
2	Cinnamoyl ferrocene	Diene polymerization	115
3	Coordination complexes with free alcoholic functions in the ligand	Polyesterification	116

I.2 Polymer formation :-

There are three principal types of reactions which lead to the formation of substances of higher molecular weight. (i) Condensation reactions which involve the elimination of simple molecules, (ii) addition reactions in which the monomeric, low molecular weight units are caused to react additively with themselves, or with other monomeric units to yield polymeric products, and(iii) Co-ordination polymerization reactions in which ligands get co-ordinated or chelated to metal atoms, and which are frequently classified under both condensation and addition polymerization reactions, but are sufficiently distinctive to warrant separate treatment. They may be strictly inorganic or inorganic-organic in character.

Reactions leading to the formation of polymers containing co-ordinated or chelated metal ions can be divided into three general catagories :-

(i) Metal-ligand chain formation :-

Polymers may result when suitable metal ions and ligands combine. The possibility of using reactions of this type depends primarily on the fact that many metal ions are poly-co-ordinate in character and can conbine with polydentate ligands. Poly co-ordinate ions are capable of accepting more than one pair of electrons and consequently, in many cases, reactions with polyfunctional (polydentate) donor molecules will result in chain or cross-linked polymeric structures.

(ii) Metal insertion in polymeric ligands :-

Some metal-containing polymers are obtained by the combination of metal ions and preformed polymeric ligands having suitable co-ordination sites.,

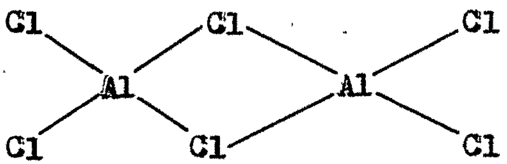
(iii) Polymerisation of co-ordination complexes or chelates :-

Some polymers are obtained when monomers containing co-ordinated or chelated metal ions are polymerized through functional groups.

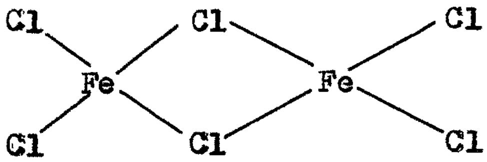
I.3 Metal-ligand chain formation :-

In theory, a ligand molecule which contains two pairs of unshared electrons can be used to link metal ions. Under certain circumstances, when the stereochemistry of the donor group and the metal ion are favourable, chelate ring formation occurs. Polymeric compounds are formed (a) when both pairs of electrons are on the same atom in the co-ordinating group (e.g. Cl, OH, NH_2), (b) when the electron pairs are on atoms linked directly to each other (e.g. -CN), or (c) when the donor atoms are widely separated in the ligand molecule.

Simplest examples of polymeric complexes formed by reaction (a) are the dimers (I and II) of the chlorides of Aluminium and Iron in the vapour state.[117] Each metal atom is surrounded tetrahedrally by four chlorine atoms.

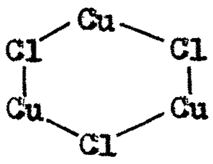


(I)



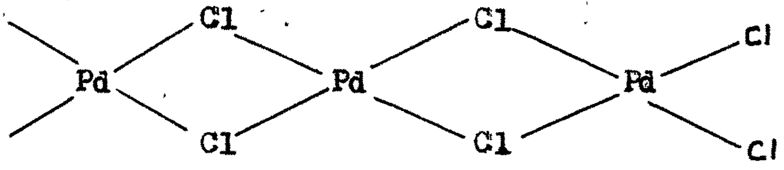
(II)

Further, copper (I) chloride is found to exist as cyclic trimer[118] (III),



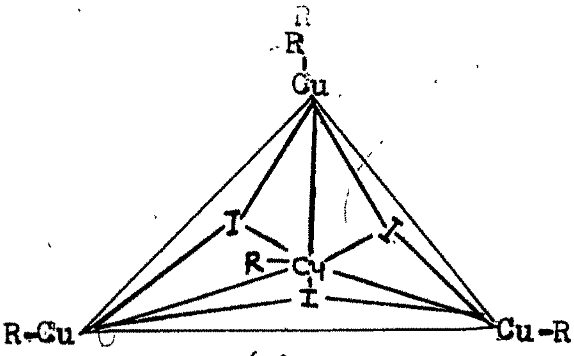
(III)

and palladium (II) chloride exists as infinite chains (IV) in the solid state.[119]



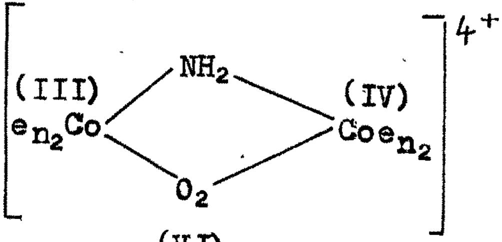
(IV)

R-Cu-I is an example which is represented as a tetrahedral cage[120] (V).



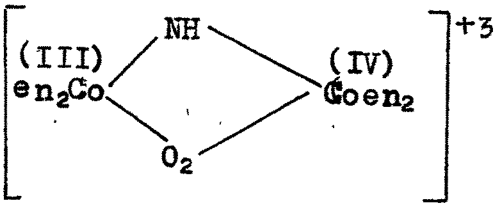
(V)

Werner isolated the first optically active dinuclear complex[121] (VI),

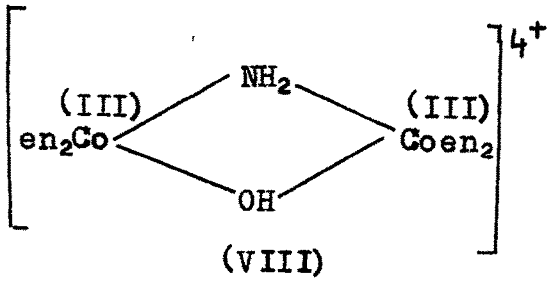


(VI)

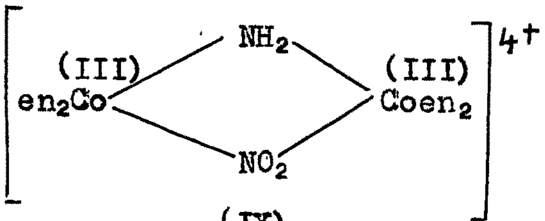
and prepared various products (VII to X) by substitution reactions.[122]



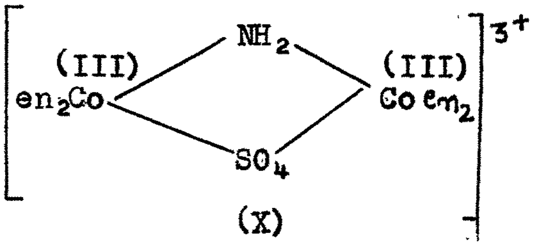
(VII)



(VIII)

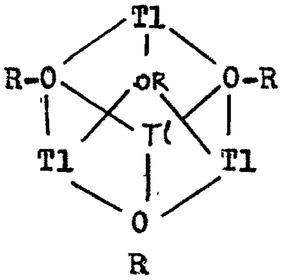


(IX)



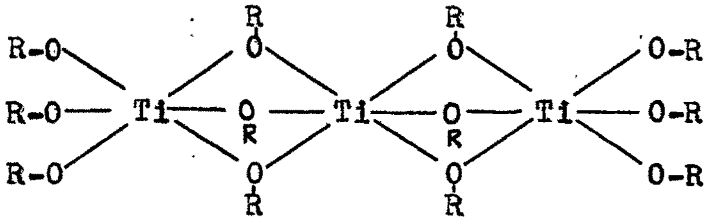
(X)

Weakly volatile covalent alkoxides of metals are considered to be polymeric. Thus thallous alkoxides are found to be tetrameric[123] (XI).



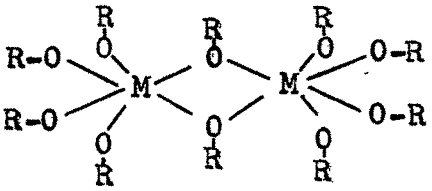
(XI)

Titanium[124] ethoxide is porposed to exist as trimer (XII) in concentrated benzene solution and,



(XII)

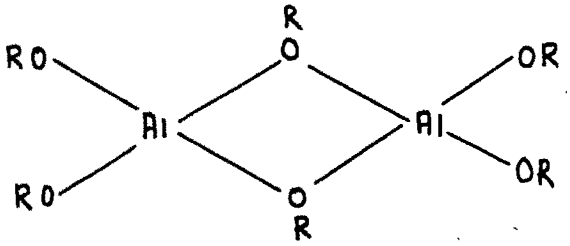
the alkoxides of Nb[125] and Ta[126] are shown to have dimeric structures (XIII).



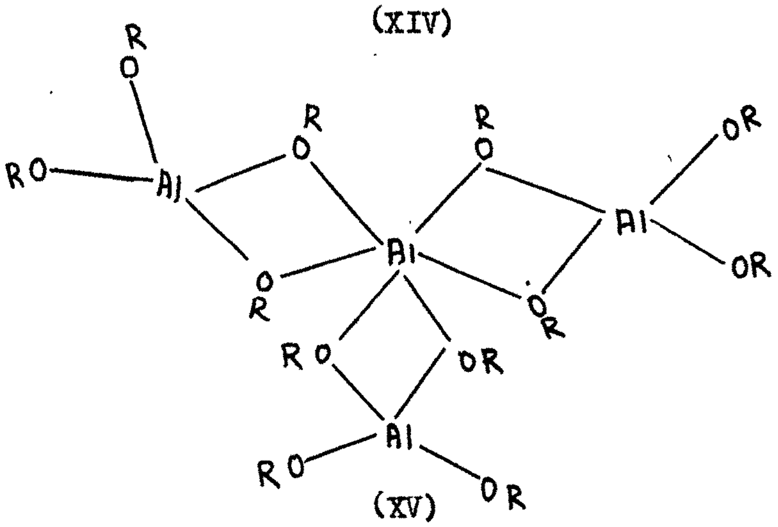
(XIII)

M = Nb, Ta

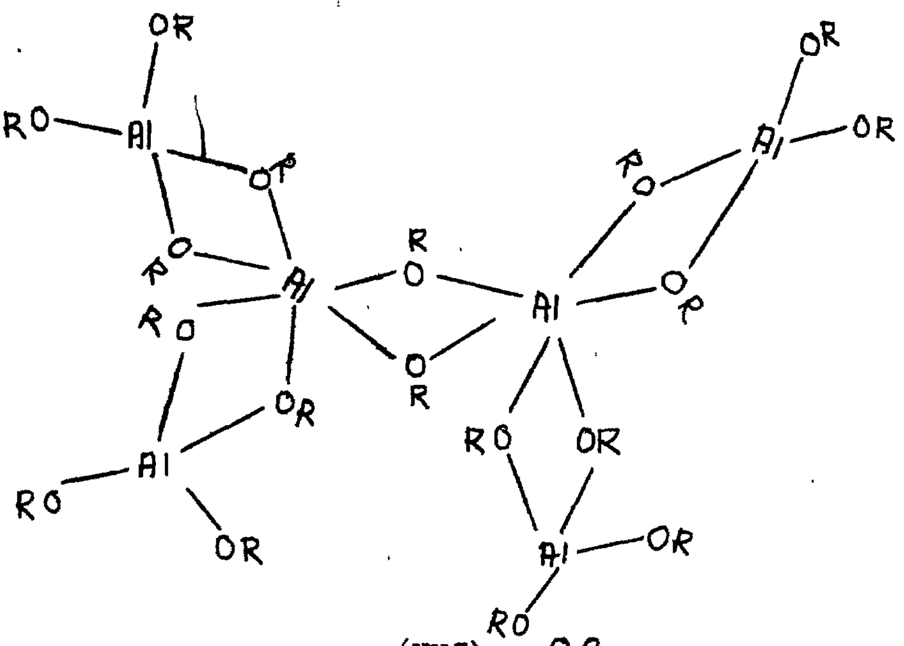
Key polymers in Aluminium alkoxides(127-30) are dimer, (XIV) tetramer, (XV), hexamer, (XVI) and octamer,(XVII).



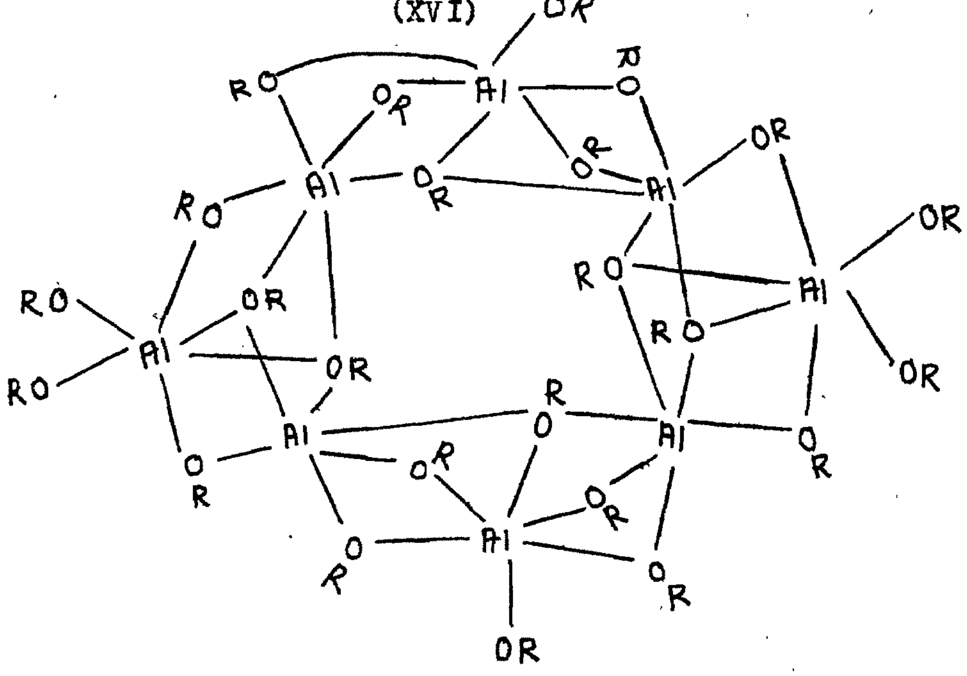
(XIV)



(XV)



(XVI)



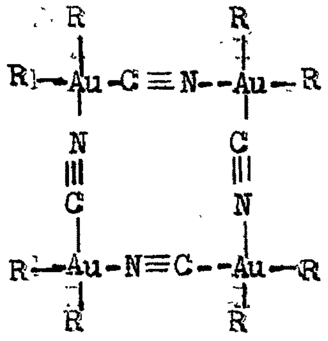
(XVII)

Metal cyanides are the familiar examples of polymers formed by reaction (B). Thus Silver cyanide is a linear polymer[131] (XVIII),

$$-(\text{--Ag--C}\equiv\text{N--Ag--C}\equiv\text{N--})_n$$

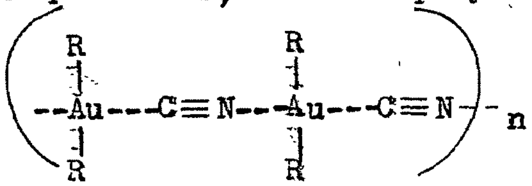
(XVIII)

and R Au CN is represented as a cyclic tetramer[132] (XIX)



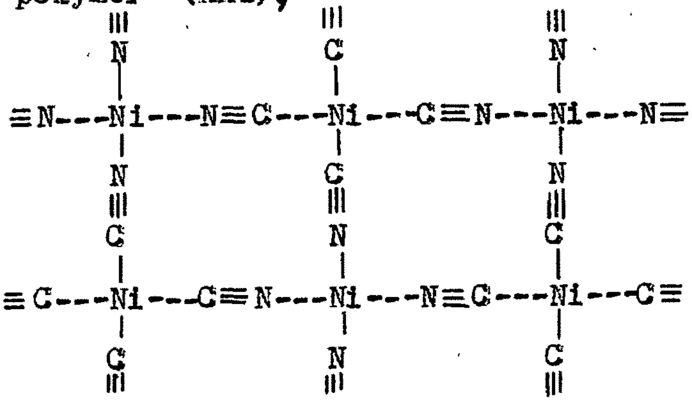
(XIX)

however, if R (alkyl) groups can be made to occupy trans instead of cis positions, a linear polymer (XX) would result.



(XX)

Nickel (II) cyanide is an example of planer, sheetlike polymer[133] (XXI),



(XXI)

and clathrate type complexes formed by nickel (II)cyanide exemplify the regular, infinite three dimensional polymers.

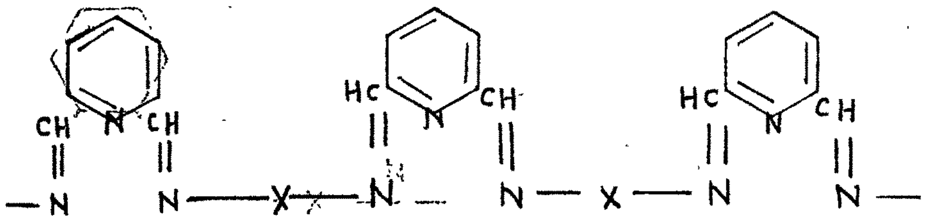
Co-ordination polymers obtained by reaction (G) are numerous and are listed in tables 5-8. It has been observed in many cases that chelation with metal ions greatly enhances the thermal stability of organic ligands. Monomeric chelate compounds are obtained with bidentate ligands such as ethylenediamine but polydentate agents can give rise to polymeric compounds. The degree of crosslinking in any polymer of this type is governed by the co-ordination number of the metal and the number of co-ordinating centres of the ligand. Combination between a bis-(bidentate) ligand and a tetraco-ordinate metal ion, or between a bis(tridentate) ligand and a hexa co-ordinate metal ion will lead to a linear polymer if the two bidentate or tridentate functions of the ligand are unable to co-ordinate with the same metal ion. A bis-(bidentate) ligand and a hexaco-ordinate metal ion or a polyfunctional ligand with a tetraco-ordinate metal ion, on the other hand, can give highly crosslinked polymeric products. A hexaco-ordinate metal can be used with bis-(bidentate) ligands to prepare linear polymers by blocking two of the co-ordination positions with other groups.

Tetra co-ordinate metal ions such as Cu(II) and Ni(II) are treated with bis-(bidentate) ligands such as 2,5-dihydroxy p-benzoquinone, napthazarin, quinizarin, anthrarufin, 5,8-dihydroxy quinoxaline, 1,5-dihydroxy phenazine, dioxime of 1,5-diacyl-2,6-dihydroxy naphthalene, bis-(acetylacetone), bis-(salicylaldehyde), rubeanic acid, etc., to get linear polymers. Cross-linked polymers were obtained in most of the cases when 6-co-ordinate M(III) and 8-co-ordinate M(IV) were used with the above ligands and no co-ordination position was blocked by other ligands.

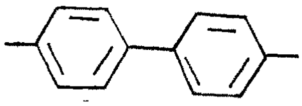
Many of the products that have been obtained at the present time from the above processes have expected thermal characteristics but are very brittle. To some extent this can be related to the highly directional nature of the bonding between the ligand and the metal ions.

I.4 Metal insertion in polymeric ligands :-

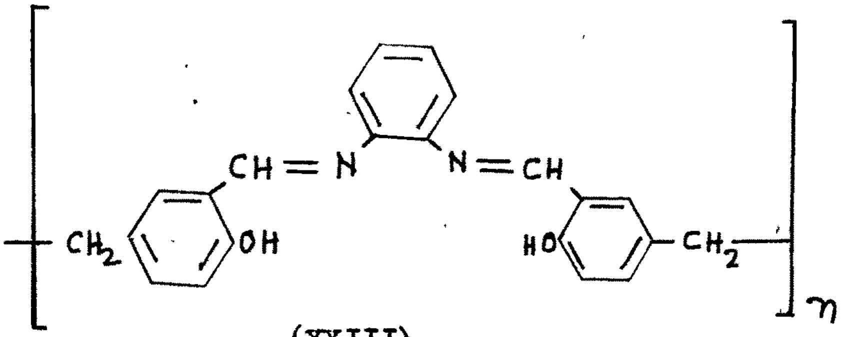
Co-ordination polymers obtained by metal insertion in polymeric ligands are listed in table-9. Production of polymers using preformed polymeric ligands has not yet been studied to any great extent. The literature, however, contains some interesting applications of this second general method. An interesting and well known example of this is the tanning of leather by metal ions, which involves, the cross-linking and stabilising of polypeptide polymers by co-ordination. Lions and Martin[102] prepared polydentate ligands by the reaction of pyridine-2,6 dialdehyde and diamines such as ethylene diamine, hexamethylene diamine and benzidine. The ligands, considered to have the structure (XXII)



(XXII)

where X is $-(CH_2)_2-$, $-(CH_2)_6$ or 

give polymers of unknown molecular weights where treated with bivalent copper or iron salts. Similarly Marvel and Tarkoy[102] prepared polymeric schiff bases with molecular weights in the region of 10,000. For example, treatment of 5,5'-methylene-bis-(salicylaldehyde) with -o-phenylene-diamine gave the poly Kis(tetradentate) ligand, (XXIII)

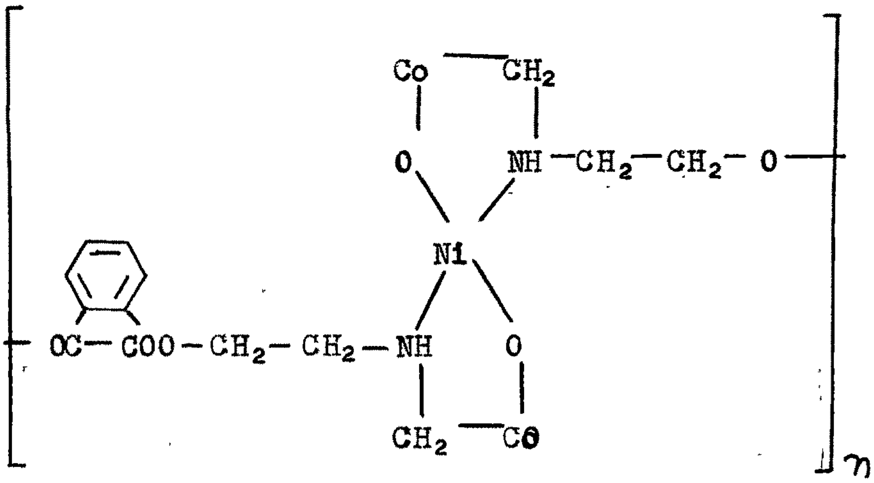


(XXIII)

which gave polymetallic chelates with Cu (II), Zn (II), etc. Analogous reactions were carried out by Bayer[134] using polymeric schiff bases obtained from glyoxal and either 2,6-diamino-p-cresol or 2,4,6-triaminophenol. It is also possible that some of the naturally occuring polymers (e.g. certain polypeptides and polysaccharides) can function similarly but interaction with ions has not been examined extensively from this point of view. However, Mester[135] has shown that formazanes obtained from polysaccharides are capable of complexing with metal ions.

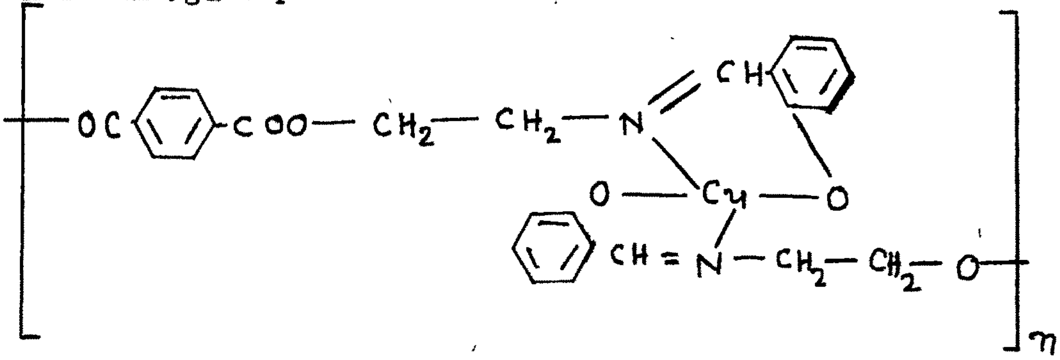
I.5. Polymerization of monomeric co-ordination complexes :

Co-ordination polymers obtained by polymerization of monomeric co-ordination complexes are listed in table-10. Higher molecular weight compounds can be prepared from co-ordination complexes when the ligand contains functional groups capable of undergoing conventional addition or condensation reactions. If the ligand contains an ethylenic side-chain, the usual addition polymerization may be possible. Vinyl ferrocene has been shown to undergo homo and co-polymerization with vinyl monomers and dienes[114] and although trans cinnamoryl ferrocene does not homopolymerize, a variety of copolymers have been obtained.[115] On the other hand, Bailar and Co-workers[116] have carried out polyesterification of co-ordination compounds having alcoholic functions in the ligand. The reaction between nickel bis-(p-hydroxy ethyl glycine) and phthalic anhydride in vaccum at 170° C gave low molecular weight polymer (XXIV),

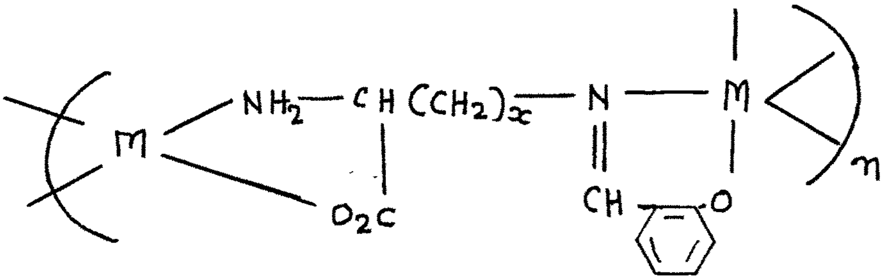


(XXIV)

while dimethylterphthalate and copper bis-salicylidene ethanolamine)gave product with structure (XXV).



Rau[136] obtained short chain polymers (XXVI) by heteropolymerization of metal-containing monomers, and Chen[137] showed that chain-length can be increased by digestion of the product.



(XXVI)

I.6 Design of co-ordination polymers-factors :-

Some of the factors[131] which are considered important in the design of stable co-ordination polymers are listed below :-

(i) The co-ordinate covalent bonds in co-ordination compounds are never purely covalent, but retaining enough ionic character to allow depolymerisations, rearrangements and displacement reactions to take place. It may also be pointed out that because of the partial ionic character of most of the co-ordinate covalent bonds, the metals in complexes commonly retain some positive charge, leaving the donor atoms with negative charges. If these charges are large, they bind the polymer chains together, and flexiblity is lost.

(ii) Hydrolytic stability of a complex is quite unrelated to its thermal stability and its ability to resist oxidation.

(iii) It should not be expected that a co-ordinated metal atom will influence the stability of chemical bonds which are not closely associated with it.

(iv) If the ligand is a neutral molecule, the polymer will be an ion, bearing a positive charge on each unit of the polymer chain equal to that of the co-ordinated metal ion. In general, greater thermal stability is attained, if these charges are internally neutralised by the use of polymer-forming ligands, which contribute negative charges equal to the positive charge on the metal ions, or by some other co-ordinated groups of proper negative charge.

(v) The stereochemistry of the metal ion and the ligand will determine whether a complex can be formed, how stable it can be, and if polymerise whether it will be linear or cross-linked.

(vi) The stabilising influence of chelation will be evident in co-ordination polymers as in metal complexes.

I.7 Aim and object of the present work :-

Interest in the field of co-ordination polymers can be for various reasons. Elliot[176] prepared highly cross-linked complexes of transition metals with bis (α-aminoacids), etc. with the hope getting highly coloured, stable materials which would serve as paint pigments. Amon and Kane[136] patented the use of linear polymers of copper and nickel with dithiooxamide as polarising media. Wilkins and Wittbecker[33] studied the formation of plastic polymeric material from the reaction of bis(β-diketones) and four co-ordinate metals (e.g. Be). Defence interest for

the production of polymers of high thermal stability or semiconducting property has given much impetus to the present day investigations.
It is known that in many cases, the organic material is stabilised against thermal or chemical attack by co-ordination with a metal ion. Thus the schiff base of acetylacetone and ethylenediamine shows no marked thermal stability, but its copper complex is only slowly decomposed at red heat.[139] It is considered possible to build heat-resistant co-ordination polymers from less stable suitable organic ligands.

It may be remarked that transition metals possess catalytic activity. Decomposition of organic ligand containing less stable group may be catalysed by co-ordination of the ligand with the transition metal ion.

Further, the formation of co-ordination polymers from monomeric co-ordination complexes by polymerisation through the functional groups, may be similarly influenced by the presence of transition metal ion in the complex.

Our main aim in this field of co-ordination or chelate polymers was to synthesise chelate polymers of highly conjugated organic ligands which would possess high thermal stability and may possess semiconducting properties. It might happen that introduction of certain groups in the chains may lead to the reduced thermal stability of the polymer. It was considered that whenever polymer formation cannot be successful, monomeric complexes be prepared as model compounds for further investigations.

With the above considerations in view we planned

(a) (i) to prepare suitable multifunctional ligands

  (ii) to prepare their transition metal polymeric complexes

  (iii) to study their optical, electrical, magnetic and thermal properties, and

(b) (i) to prepare suitable monomeric co-ordination complexes and

  (ii) to polymerise them through suitable functional groups.

Investigations carried out with the above considerations in view and the results obtained are discussed in the following pages.