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POLYMERIC CHELATE COMPOUNDS

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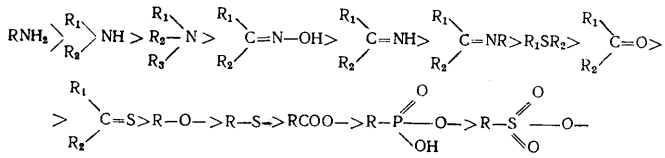
The development of modern polymer technology poses the complex problem of producing polymers possessing, in addition to high thermal stability, a high electrical conductivity, magnetic permeability, electron-exchange capacity, and many other special properties.

The solution of these problems requires the development of new routes to the synthesis of polymeric materials which possess the easy workability, chemical stability, and specific physico-mechanical properties characteristic of many organic and organometallic polymers, and the thermal stability, electrical conductivity, magnetic permeability, etc., of metals.

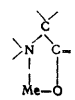
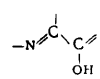
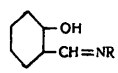
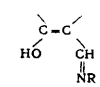
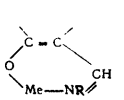
At present there are prospects of methods which might lead to new types of polymers, having a wide range of properties. Among these new methods is the synthesis of polymeric chelate complexes.

It is known[1] that chelate complexes are usually insoluble in water and show high stability towards the action of acids, alkalis, and reagents which react with the free metal ion. Many chelate complexes are very stable at comparatively high temperatures (400° or more). Compounds which form chelate complexes contain strongly polarised electron-donor and electron-accepting groups; in most cases these groups are present in a conjugated chain, which allows the unshared electrons to move towards the more electronegative atom or group.

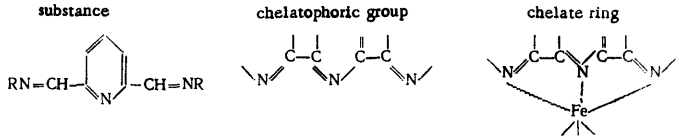
Groups which can form chelate rings are conveniently called chelatophores*. The electron-donor groups which form chelatophores may be arranged in the following series:



These groups when present in a molecule form chelate rings in the presence of an electrophilic ion or atom, the stability of the resulting rings being considerably increased if the above groups are present in a conjugated chain. This is illustrated by the following examples.

Substance	Chelatophoric group	Chelate ring
NH_2CH_2COOH		
		
		

In certain cases the complex-forming group contains more than two atoms capable of forming chelate rings with metal atoms; such chelatophores are called "tridentate" (with three such atoms), "tetradentate" (with four atoms capable of forming rings with a metal), and so on. The following is an example of a tridentate chelatophore:

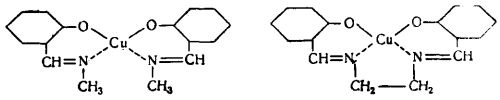


* Author's definition (Ed. of Translation).

The chemical and thermal stability of the chelate ring depends on a number of factors, including the structure and chemical nature of the chelatophore, the strain in the cyclic structures, the number of rings joined to the given ion, and the electronic structure of the complex-forming ion. Depending on the structure of the chelatophore, chelates with 4, 5, 6, 7, 8 or more atoms in the ring are formed. With a planar disposition of atoms, the five- and six-membered rings are the most stable. They are formed by the reaction of metal ions with ethylenediamine, diethylene triamine, *o*-hydroxyacids (e.g. salicylic acid and its derivatives), β-diketones (e.g. acetylacetone and benzoylacetone), 8-hydroxyquinoline, 1-hydroxyanthraquinone, etc.

According to Bayer's theory, the five-membered ring has the least strain; however, when the ring is made up of alternating single and double bonds, the six-membered ring is the most stable, since complete conjugation is then possible, with the greatest gain of energy.

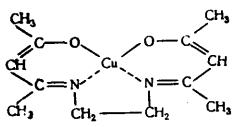
These considerations also apply in the chemistry of chelate compounds. Pfeiffer[2] has shown that five-membered chelate rings are more stable than six-membered when there are no conjugated double bonds in the resulting chelate. The more rings formed when the chelatophore reacts with the metal ion or atom, the lower will be the internal energy on the formation of the stable cyclic structures. This has been confirmed by Calvin and Bailes[3], who showed that chelate compounds in which the metal atom is a member of several rings are more stable chemically and thermally than analogous compounds with fewer rings. Thus the half-wave potential of a complex with three chelate rings is considerably lower than that of an analogous complex with two such rings; for instance, the Schiff's bases obtained from salicylaldehyde and methylamine and ethylenediamine have half-wave potentials of ±0.02 and -0.75 respectively:



The Table gives the logarithms of the stability constants for various chelates of Zn and Ca.

Chelates of Zn with:	log k (Σ log k_n)	Chelate of Ca with:	log k (Σ log k_n)
Ethylenediamine (2) rings	11.1	Methylaminodiacetic acid (4 rings)	7.5
Triethylenetetramine (3 rings)	14.6		
Aminodiacetic acid (4 rings)	13.5	Ethylenediamine tetraacetic acid (5 rings)	10.6
Ethylenediamine tetraacetic acid (5 rings)	16.6		

The presence of several rings in a chelate also makes these compounds more stable towards heat. Thus, for instance, copper ethylenediamine-bis-acetylacetonate



is hardly decomposed at red heat[5], and copper phthalocyanine sublimes in a vacuum at 570° without decomposition[6].

The stability of the complex depends on the type of bond between the metal ion and the chelatophore donor groups[7] and on the electronic structure of the ion.

There is a definite relationship between the chemical stability of the complex and the nature of the metal ion. Mellor and Maley[8] studied the stability of salicylaldehyde complexes in 1 : 1 water–dioxan. The metals lie in the series Pd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Mn^{2+}, Mg^{2+} in order of decreasing stability of the complex. Almost the same order was found by Pfeiffer[9] for the complexes of Cu, Ni, Fe, Zn, and Mg with ethylenediamine and 8-hydroxyquinoline, and by Van Uitert and coworkers[10] for the complexes of Ag^{2+}, Cu^{2+}, Be^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Pd^{2+}, Mn^{2+}, Cd^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} with β-diketones.

The chemical stability of the chelates decreases with increasing basicity of the metal; the most weakly basic metals (Pd, Cu) form the most stable complexes. Thus the chemical stability of the chelates decreases with increasing ionic character of the bond between the metal and the atoms of the chelatophoric group.

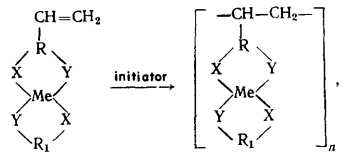
In most cases the chelate complexes are distinguished by a comparatively high chemical stability. For example, the copper salt of ethylenediamine tetraacetic acid is unchanged on boiling with alkali[11]. The stability of the chelates of the alkaline-earth metals with ethylenediamine tetraacetic acid is so great that the metals are not precipitated as sulphates, oxalates, phosphates, carbonates, etc. The glycinate and alaninate of Co^{3+} dissolve in concentrated sulphuric acid without any substantial chemical change. Beryllium salicylates are only slightly decomposed by alkalis[12].

It would be expected, from these distinctive properties of the chelate compounds, that polymeric chelates would possess many interesting properties.

From the chemistry of synthetic polymers and the theory of complex compounds, the following four methods for the synthesis of polymeric chelates (polychelates) may be considered.

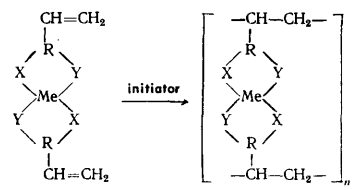
1. The polymerisation of monomers containing a metal atom joined in a chelate ring:

   (a) the formation of linear or low-branched macromolecules:



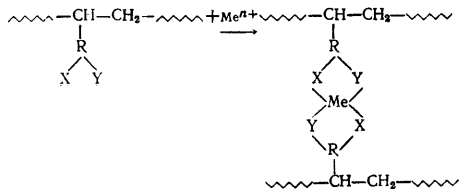
   where  is the chelatophore, Me is the metal atom, and R_1 is an aromatic, alicyclic, or acyclic radical;

   (b) the formation of three-dimensional or highly branched macromolecular structures:

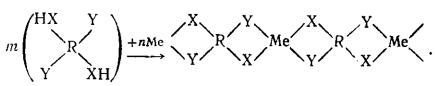


2. The synthesis of polymers by the polycondensation of substances containing chemically stable chelate rings; this can be achieved by the reaction of low-molecular substances containing chelate rings and at least two reactive groups (carboxyl, hydroxy, amino, ester, alkoxy, etc.).

3. The synthesis of polymers by the reaction of carbo- or hetero-chain polymers containing chelatophoric groups, with metal ions or atoms; soluble (linear, branched) and insoluble (cross-linked) polymers can be produced:



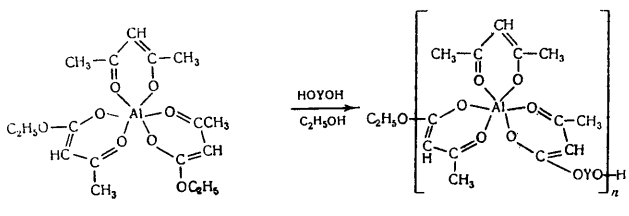
4. The synthesis of polymers from complex-forming low-molecular substances and metal ions or atoms. This method, as distinct from the preceding methods, can produce polymers in which the macromolecules are built up with covalent and coordinate bonds; such a reaction should be called polycoordination. The principle of the method is shown in the diagram[13]:



Depending on the structure of the original chelatophore and the nature of the metal ion, the polycoordination reaction can produce polymers of linear (ribbon), planar, or three-dimensional structure.

It may be expected that by combining various monomers containing chelatophoric groups, copolymeric-polycondensation and, in particular, polychelate compounds with a wide range of physical and physicochemical properties could be prepared. The use of the polycondensation reaction for the synthesis of block and graft copolymers is also of great interest.

At present, the synthesis of polymeric chelate compounds is in the initial stage of development. There are as yet no published references to the preparation of such polymers by type 1 reactions. Polymers containing aluminium chelates have been prepared by a reaction of the second type. Patterson and coworkers[14] have prepared polymeric chelates of the following structure by the condensation of diols with monomeric aluminium chelates containing groups capable of further reaction:



where HOYOH is a diol.

The resulting polymers are solid transparent coloured substances, soluble in benzene. They can be drawn from a melt into long brittle fibres, but have low thermal stability; they all decompose above 200°.

TABLE 1. Properties of the polychelates obtained by the reaction of aluminium acetylacetonate bis-(ethyl acetoacetate) with diols.

Diol	Softening temp. of the polymer, °C	Molecular wt. of the polymer
Ethylene glycol	105—120	1370* 2020**
Diethylene glycol	105—110	980**
Triethylene glycol	75—130	1100**
Butane-1,3-diol	100—110	2620*
Butane-1,4-diol	95—150	940**
Pentane-1,5-diol	80—100	1570**

* Molecular weight determined by acetylation of the end groups.

** Cryoscopic method in benzene.

Attempts to produce polymers of higher molecular weight by heating these polymers in a vacuum at 200°–250° failed, since under these conditions acetylacetone is split off and no cross-etherification takes place.

Polymeric chelates have also been prepared by the condensation of diisopropylaluminium monoacetylacetonate with a number of compounds containing two chelatophoric groups. These compounds are similar to those described above; they also do not have a high thermal stability, decomposing with the liberation of acetylacetone above 200°. Some of these polymers are insoluble and do not melt, which is explained by the great rigidity of the main polymer chain:

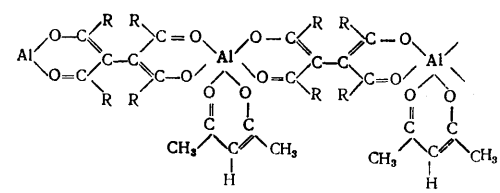


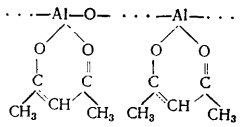
TABLE 2. Properties of the polymers obtained by the condensation of diisopropylaluminium monoacetylacetonate with various compounds.

Compound	Form of the polymer	Softening temp. of the polymer, °C	Molecular wt. of the polymer
Ethylene-bis-(acetoacetate)	solid yellow transparent	130—150	770
Diethylene-glycol-bis-(acetoacetate)	»	80—150	930
Tetramethylene-bis-(acetoacetate)	pale-yellow, transparent	75—95	1160
Pentamethylene-bis-(acetoacetate)	»	40—45	450
2,4-Diacetylresorcinol	rust-brown *	>360	—
2,2'-Bis-(ethyl-acetoacetate)	»	>360	1860
1,1,2,2-Tetraacetylethane	granular, white	>360	—
1,1,2,2-Tetrabenzoylethane	mainly original substance separated		
α,α-Methylene-bis-(ethylacetoacetate)	brittle brown	110—130	1275
1,1,3,3-Tetraacetylpropane	dark red, transparent	90—150	1070
1,1,3,3-Tetrabenzoylpropane	brittle, amber colour	130—145	920

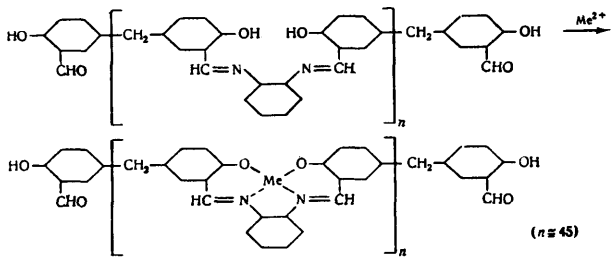
* Insoluble in organic solvents.

All the polymers apart from the one marked with an asterisk (Table 2) are soluble in benzene; molecular weights were determined cryoscopically.

The high-temperature hydrolysis of dialkoxyaluminium acetylacetonate[15] is the same type of reaction. It is known that this interesting reaction takes place with the loss of two molecules of alcohol for each molecule of complex, forming a polymeric product, probably having the structure

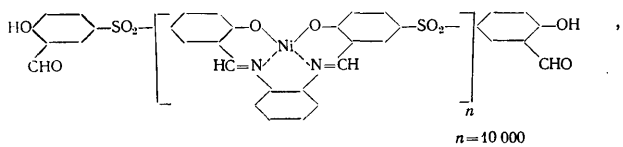


Marvel and Tarkoy[16] have recently described the conversion of carbo- or hetero-chain polymers containing chelatophoric groups into a polymeric chelate compound (reaction 3). The starting material was the Schiff's base obtained from methylene-(bis-salicylaldehyde) and *o*-phenylenediamine; the reaction of this polymer with acetates of Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Fe^{2+} in a mixture of tetrahydrofuran with water or acetic acid produced a polymer with chelate linkages.



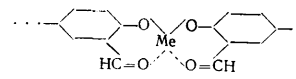
These polymers are insoluble and vary in colour from orange to dark brown, depending on the metal. The thermal stability of the polymers also depends on the metal, and increases in the series: Cu, Co, Zn, Ni, Fe, Cd. On heating at 250° for 3 h these polymeric complexes lost 11–26% of their weight, partly because of the loss of water of crystallisation (1–2 moles of H_2O per atom of metal).

Increased thermal stability as compared with the polymers prepared by Marvel and Tarkoy[16] is found if the methylene groups are replaced by sulphone groups $-SO_2-$;[17] thus the polymers based on the polymeric Schiff's base from bis-(salicylaldehyde-5,5-sulphone) and *o*-phenylenediamine:



lose only 0.3% of their original weight on heating at 250° for 3 h.

It is interesting that the thermal stability of the compounds mentioned above is almost independent of whether it is measured in air or in nitrogen, indicating that these compounds are relatively stable to oxidative destruction. It may be assumed that the polymeric chelates of the above structure can form their own block polymers because of the existence of the terminal hydroxy and aldehyde groups; the metal atom joins separate macromolecules with the formation of longer chains:



The formation of insoluble chelates of Cu, Zn, Fe, Sn, and other metals with the linear polymers obtained by the reaction of salicylaldehyde with polyamines has been reported[18].

Among the polymers with chelate bonds are the salts of polymethacrylic and polyacrylic acids with Cu^{2+} [19-21] and other metals. Various methods of studying these polymeric complexes have shown that the copper atom is linked to two or four carboxyl groups[19,20,22-24]. These complexes are considerably more stable than complexes of the monomeric analogue, glutaric acid[24], probably because of the influence of the polyelectrolyte field or the presence of vicinal structures in the polyacrylate chains.

It is interesting that polymers containing isolated carboxyl groups show only a slight adsorption of Cu^{2+}, La^{3+}, Mg^{2+}, and K^+,[25] as compared with the adsorption of Cu^{2+} by polymethacrylic acid.

Polyacrylic acid forms complexes with Mg^{2+}, Ca^{2+}, Co^{2+}, Mn^{2+}, and Zn^{2+}.[26] The ions of Ca, Sr, and Ba cause gelatinisation of solutions of polyacrylic acid, the activity of the ions falling in the series: Ba, Sr, Ca.[27] The ions Ni^{2+}, Co^{2+}, and Zn^{2+} have a low tendency to complex formation with polyacrylic acid[20].

The ability of acrylic acid polymers and copolymers to form stable non-melting and insoluble compounds with ions of di- and polyvalent metals had already been found in 1946 by Berlin[28], who suggested this reaction for the preparation of thermally stable plastics.

Morawetz and coworkers[29] studied the chelates of Mg, Ca, Sr, and Ba with hydrolysed copolymers of maleic anhydride and styrene or vinyl ethyl ether.

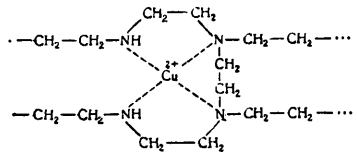
The polymeric keto-ester obtained by the hydrolysis of poly(ethyl-3-ethoxy-2,4-pentadienoate) complexes with Cu^{2+} is a pale green solid which does not melt up to 205° (the original polymer has m.p. 90°–125°) and which is insoluble in solvents which dissolve the original polymer[30].

The preparation and properties of polyvinyl acetoacetate[31] and the polychelates from polyvinylacetonylketone with salts of Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, UO_2^{2+}, Pr^{3+}, and Nd^{3+},[32] have been described.

After treatment with alkali, the copolymer prepared from methacrylylacetone (2-methylhex-1-ene-3,5-dione) and 10% ethylene glycol dimethacrylate in the presence of 1% azodiisobutyronitrile adsorbs Fe^{2+} and UO_2^{2+} ions at definite pH values below 7. The ability to extract Fe^{2+} and UO_2^{2+} ions is also possessed by the copolymers prepared from methacrylylacetone and methacrylic acid in the ratio 1:1 or 1:2 and 10% ethylene glycol dimethacrylate in the presence of azodiisobutyronitrile and water. These resins easily exchange iron and uranyl ions and have been suggested for use as ion-exchange resins[33].

Chelate compounds are also formed by the reaction of monovalent copper ions with polyacrylonitrile and its copolymers[34-37], the copper ions forming complexes of coordination number 4 with the cyano groups of polyacrylonitrile.

The phenomenon of complex formation is widely used for the selective extraction of metals with ion-exchange resins. Polyethylene-imine cross-linked with dibromoethane forms stable complexes with divalent copper and less stable complexes with Co^{2+}, Ni^{2+}, and Zn^{2+}:[38,39]



For the extraction of metals, Gregor and coworkers[40] synthesised a number of resins from *m*-phenylenediglycine and formaldehyde, anthranilic acid, resorcinol, and formaldehyde, and *o*-aminophenol and formaldehyde[40,41]. These resins form complexes with Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} at pH 5, the resin from anthranilic acid extracting the metals to a lesser degree, probably because of the presence of a very fine lattice.

Parrish[41] prepared a resin from resorcinol, pyrogallol, and formaldehyde which forms complexes with Ba^{2+}, Ca^{2+}, and Sr^{2+}. He also prepared a resin by diazotising the *o*-aminophenol resin and coupling with 2-naphthol; this complexes with Mg^{2+} and Cu^{2+} at pH 3. An *o*-aminophenol--formaldehyde resin, obtained by reducing the *o*-nitrophenol-formaldehyde resin, complexes easily with Cu^{2+} in the presence of Ca^{2+} at pH 5.5.

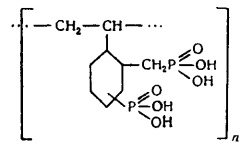
Diazotisation of an amino resin and coupling with 8-hydroxyquinoline enabled Parrish[42] to synthesise a product which adsorbs the ions of various metals at different pH values; at pH 2–3 it adsorbs Cu^{2+}, Ni^{2+}, and Co^{2+}, and at pH 1.5, 2.0, 2.8, 4.0, and 4.8 it adsorbs Zn^{2+}, Mn^{2+}, Al^{3+}, Mg^{2+}, and Ca^{2+} respectively.

The coupling of diazotised polyaminostyrene with *o*-hydroxyphenylarsonic, salicyclic, or kojic acids, enables ion-exchange resins having an affinity for copper ions to be obtained. Similar resins are prepared by condensing resorcinol with formaldehyde and certain acids[43]. Resins which selectively extract heavy metal ions are obtained by condensing a mixture of resorcinol and anthranilic acid (or 8-hydroxyquinoline) with formaldehyde[44].

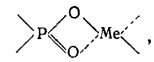
The polythiols obtained by hydrolysing the reaction product of thiourea with chloromethylated polystyrene selectively adsorb Hg^{2+} in the presence of Mg^{2+} at pH 7.[42]

The introduction of complex-forming substances enabled Klyachko[45] to synthesise resins which selectively extract metal ions. Thus by condensing phenol sulphonic acid with formaldehyde and ethylenediamine tetraacetic acid a resin is obtained which selectively extracts Ca^{2+}. The introduction of dimethylglyoxime into a sulpho-resorcinol cation--exchange resin gives a resin which complexes with Ni^{2+}. The addition of 1,8-dihydroxynaphthalene-3,6-disulphonic acid in the preparation of sulpho-phenol cation-exchange resin gives a resin which forms chelates with titanium, gold, vanadium, and other metal ions.

The work of Kennedy and coworkers[46–48] on the phosphorylation of chloromethylated styrene cross-linked with divinylbenzene is of considerable interest; the resulting polymers contain the group:



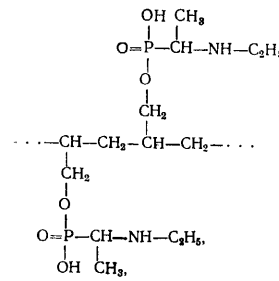
and form four-membered chelate rings with metal ions:



the activity of the resin towards various ions decreasing in the series:

$$Th^{4+} \text{ and } U^{4+} > UO_2^{2+} \cong Fe^{3+} > \text{rare earths}^{3+} > H^+ > Cu^{2+}, Co^{2+}, \text{ and } Ba^{2+} > Na^+.$$

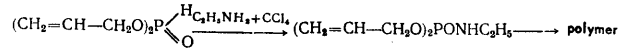
Treating polymeric diallyl phosphate with acetaldehyde-ethylene-imine with subsequent hydrolysis gives polymers containing the chelatophoric groups



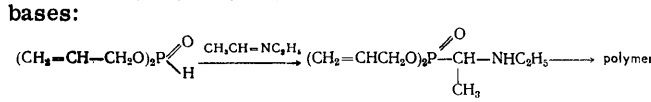
and these form stable complexes with ions of metals of variable valency[46–48].

Kennedy, Lane, and Robinson[47] have prepared a number of phosphorylated polymers by the partial hydrolysis of polymeric allyl phosphates, by the reaction of polyvinyl chloride or channel black with PCl_3 in the presence of $AlCl_3$, and by treating phenol-formaldehyde resin with tetraethylpyrophosphate in alkaline medium.

Kennedy and Ficken[48] synthesised polymeric phosphonamides and α-aminophosphonates by the reactions:

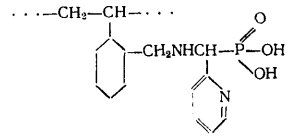


Poly-α-aminophosphonates were prepared from polymeric diallyl hydrogen phosphonate by reaction with Schiff's bases:



A series of polymers was prepared in this way; complex-forming groups are formed on partial hydrolysis.

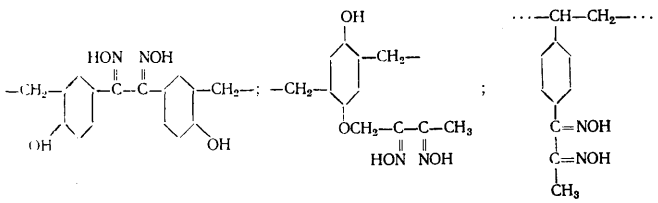
Polyaminomethylstyrene gives with pyridine-2-aldehyde a polymer which reacts with diethyl hydrogen phosphonate; hydrolysis of the resulting product gives a polymer which is capable of forming complexes:



Resins which form polychelates are obtained by condensing with formaldehyde the reaction products of salicyl or resorcyl aldehyde with dialkyl phosphites or phosphoric acid[49].

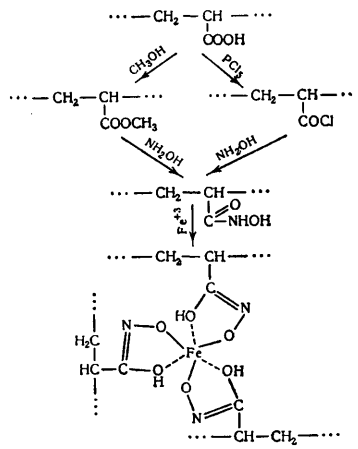
Phosphorylated cellulose is used for the chromatographic separation of Cu, Fe, and Ni ions and the partial separation of Au, Pd, Pt, and Rh[50]. Other phosphorylated resins also form complexes with metal ions[51,52]

Štamberg, Seidel, and Rahm[53] have synthesised three polymers which selectively extract Ni^{2+}; they have the structures

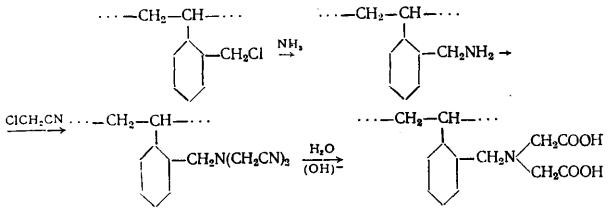


Polymers which complex with Fe^{3+} and selectively extract these ions from solution have been prepared by Cornaz and Deuel[54] and Hale[55] from polymeric carboxylic acids and by Kern and Schulz[56] from polyesters.

The formation of polyacrylic-acid derivatives containing chelatophoric groups and the structure of the chelates obtained from them may be represented as follows:

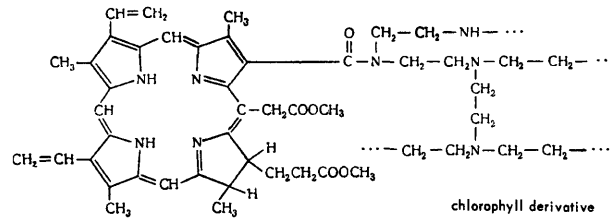


Chloromethylated polystyrene can be converted into a polymer which complexes with the alkaline-earth metals and serves for their extraction[41]:



Similar resins which complex with Cu^{2+} have been prepared from chloromethylated polymers by reaction with various aminoacids, for example methylaminodiacetic acid, dimethylaminoacetic acid, methylethanolaminoacetic acid, etc.[57].

Polymers containing chlorophyll and haemin residues are interesting examples of polymeric materials which form chelates; such substances form stable complexes with Fe^{2+} [58,59].

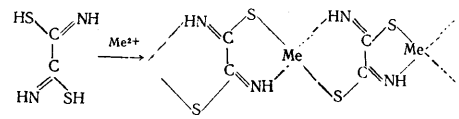


The copolymers of 2-vinyl- and 2,4-divinylhaemins with styrene[60] are of great interest in this respect.

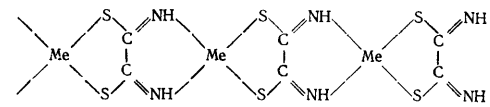
It is seen that by suitable reactions it is possible to synthesise various polymers which are capable of forming complexes with metal ions, and so obtain a large number of various cross-linked polychelates which are of considerable practical interest as ion adsorbents.

One of the most interesting, but little developed, methods of synthesis of polymeric chelates is the polycoordination reaction of low-molecular compounds containing chelatophores. Inorganic and organic polymers can be prepared by this reaction.

Jensen[61] describes the polymeric chelates of dithiooxamide (rubeanic acid) with Ni^{2+} and Cu^{2+}:



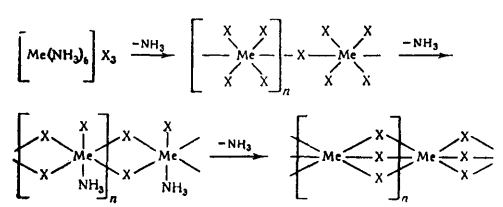
Study of their infra-red spectra shows the presence of the NH bond[62]. From X-ray spectrographic studies of crystalline rubeanic acid, this polymer is given the *trans*-structure; however, Xavier and Ray[63] suggest that the polymer may exist in the *cis*-form:



The polymeric compounds of rubeanic acid with copper are insoluble in water; the Ni, Co, and Pd polychelates are soluble in pyridine.

It has been found that films coated with rubeanic-acid polychelates pass light in one direction only, apparently because of the parallel orientation of the polymer chains[64].

In 1956 Schmitz-Dumont[65] reported the preparation of the polymeric complexes

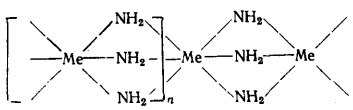


where Me = Co^{3+} or Cr^{3+}, and X = NO_3.

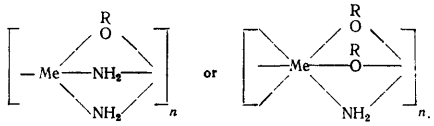
Replacing the residue X by the NH_2 group gives the metal amides

$$[Me(NH_3)_6](NO_3)_3 \xrightarrow{KNH_2} [Me(NH_3)_6](NH_2)_3 ,$$

which, on losing NH_3, are converted into polymeric complexes



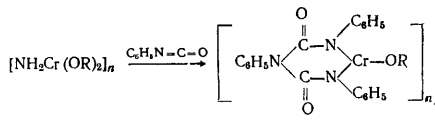
By splitting out alcohol and NH_3 from Co(III) or Cr(III) hexammine alcoholate, polymeric complexes are obtained of the type



The synthesis of inorganic polymeric complexes is an example of polycoordination in which other products are also liberated, i.e. it is analogous to polycondensation. All the complex polymers reviewed above are amphoteric, reacting with both NH_4X and KNH_2 in liquid NH_3.

The polymeric metal amides react with diphenylketene and phenyl isocyanate[65]:

$$[NH_2Cr(OCH_2C_6H_5)_2]_n + n(C_6H_5)_2C{=}C{=}O \rightarrow [(C_6H_5)_2CHCONHCr(OCH_2C_6H_5)_2]_n$$



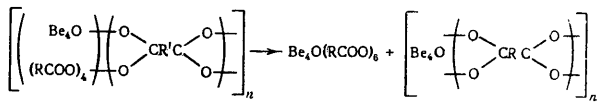
The reaction of organic phosphorus compounds with MoO_3 and 90% H_2O_2 gives polymeric complexes which are stable up to 150°–160°,[66] the structure of which cannot be considered as definitely established.

In 1940 Holland[67] reported the formation of polymeric complexes of chromium with succinic, fumaric, glutaric, suberic, adipic, azelaic, and phthalic acids, and in 1950 Shuttleworth[68] confirmed this.

The basic beryllium carboxylates $Be_4O(RCOO)_6$, which are covalent compounds, possess a fairly high thermal stability, and can be sublimed without decomposition at atmospheric pressure above 300°–350°. In 1907 Tanator and Kurovskii[69] prepared basic beryllium succinate, but it was not identified as a polymer, although it is a solid infusible glass, and is probably of three-dimensional structure.

Marvel and Martin[70] (1958) studied the possibility of, and the conditions for, the replacement of the monocarboxylic acid residues in the basic beryllium carboxylates by dibasic acid residues with the object of obtaining thermostable polymeric materials. Equimolecular quantities of beryllium acetate, propionate, or benzoate and adipic, β-ethyladipic, sebacic, isophthalic, or terephthalic acid dichlorides were heated in toluene or other solvent for 16–20 h, and the polymer precipitated with petroleum ether. All the polymers are powders with a degree of polymerisation of 4–6.

The polymers containing only aliphatic acids possess limited elasticity on plasticising with a small amount of solvent, and can be drawn into short filaments. They are not decomposed above 400°, but the linear polymer disproportionates to form three-dimensional structures; this takes place even at room temperature:

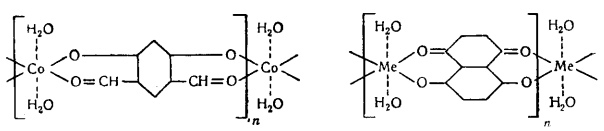


The polymers containing aromatic acids are somewhat more stable to disproportionation, but at 340° they also disproportionate quite readily.

Insoluble three-dimensional polymers are obtained when the polycoordination is carried out by fusing basic beryllium propionate with sebacic, adipic, and terephthalic acids.

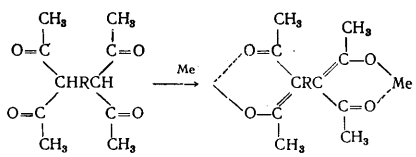
Polymeric beryllium carboxylates have also been prepared by polymerising beryllium methacrylate pentapropionate and beryllium hexamethacrylate in the presence of benzoyl peroxide, but the polymer derived from the former was only very slightly soluble. Both substances are white powders which decompose vigorously at 200°. The low thermal stability of such polymers is probably due to the presence of the main carbon chain; however, poly-beryllium methacrylate pentapropionate is more stable to heat than many polymethacrylic and polyacrylic esters.

Polymeric complexes of Co^{2+} with 4-hydroxy-5-formylsalicyl aldehyde[71], of Co^{2+} and Be^{2+} with naphthazarin[71,72], and of Cu^{2+}, Fe^{2+}, Hg^{2+}, and Ag^{2+} with 2,5-dihydroxybenzoquinone[73] have been described:



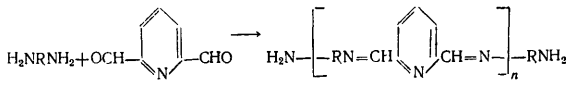
where Me = Co^{2+} or Be^{2+}.

In 1954 Wilkins and Wittbecker[74] proposed a new method for the production of thermostable polymers suitable for the preparation of fibres, films, and coatings, by the reaction of tetraketones with salts of the divalent metals Be, Cu, Ni, Zn, Co, Fe, Pb, Mn, Ca, Ba, Sr, and Cd. The polycoordination reaction can be effected by heating a mixture of a tetraketone and beryllium acetylacetonate at 200°, the acetylacetone liberated being distilled off. Suggested tetraketones are terephthaloyl bis-acetone, *p*-bis-(2,2-diacetylethyl)benzene and bis-(*p*-acetoacetyl)phenyl ether:

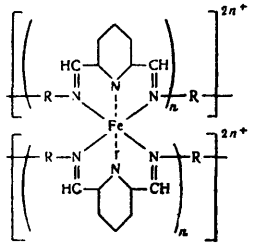


The polymeric chelate compound from terephthaloyl bis-acetone has a melting point above 285° and is insoluble in boiling benzene and dimethylformamide. The polymeric complex from bis-(*p*-acetoacetyl)phenyl ether is insoluble in a mixture of methanol and chloroform.

Lions and Martin[75] obtained infusible polymers by the polycondensation of pyridine-2,6-dialdehyde with ethylenediamine, hexamethylenediamine, and benzidine:



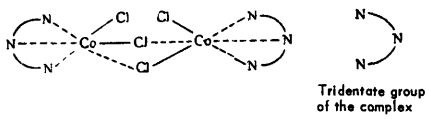
The polymer derived from benzidine possesses a very slight tendency to coordinate with Fe^{2+}, but forms polychelates with $CuCl_2$. The polymers from ethylenediamine and hexamethylenediamine react easily with Fe^{2+} on boiling an aqueous suspension of the polymer with excess $FeSO_4$, forming dark red products which are insoluble in the usual solvents and are not decomposed or melted up to 300°; they have the structure:



i.e., each metal atom combines with two tridentate residues of the polymer. This polymer has very unusual magnetic properties — it is ferromagnetic with molar magnetic susceptibility $155\,000 \times 10^{-6}$ cgs units.

In the preparation of the polymeric chelate by reacting pyridine-2,6-dialdehyde with ethylenediamine in the presence of $FeSO_4$ in aqueous alcoholic solution, a soluble polymer is formed, in which two iron atoms are combined with seven tridentate residues. The perchlorate of this polymer has diamagnetic properties. The authors find it difficult to explain such unusual magnetic properties in these polychelates.

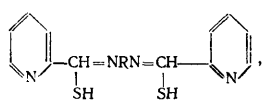
The reaction of the polymeric Schiff's base with Co^{2+} salts ($CoCl_2$) produces a paramagnetic polymer in which each tridentate group combines with one cobalt atom (magnetic movement, 3.7 Bohr magnetons). This polymer is given the structure



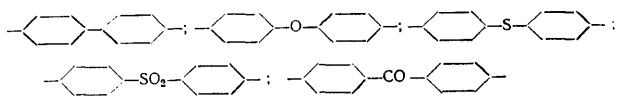
Tridentate group of the complex

the existence of chlorine bridges being assumed.

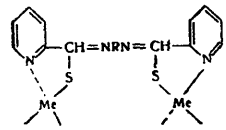
In 1958 the synthesis of polymers of chelates based on bis-α-thiopicolylamides was reported[13].



where R =



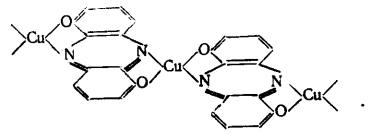
They are prepared by mixing stoichiometric quantities of a solution of bis-α-thiopicolylamides in dimethylformamide and a methanolic solution of metal (Cu, Ni, Zn) acetates, the polymer precipitating almost immediately. To complete the reaction the solution is heated for half an hour. The polymeric chelates are insoluble in organic solvents and do not melt below 300°. Analysis and their infra-red spectra confirm the structure



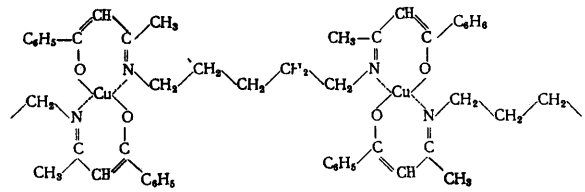
where Me = Cu^{2+}, Ni^{2+}, or Zn^{2+}. These polymers have a low molecular weight of the order of 15 000. The same result is obtained if the polycoordination is carried out by heating a mixture of equimolecular quantities of the metal acetylacetonate and the bis-α-thiopicolylamide in vacuum.

The bis-α-thiopicolylamide polymers prepared from p-diaminobenzophenone and p-diaminodiphenylsulphone are the most stable thermally. The polychelates of Cu^{2+} and Ni^{2+} are stable up to 300°, and the Zn^{2+} polychelate is stable up to 370°, the loss in weight at this temperature being less than 3.5%. The higher thermal stability of the zinc-containing polymers is due to zinc having only one state of oxidation. Metals of variable valency may be oxidised on heating, and the resulting oxides probably catalyse the thermal decomposition.

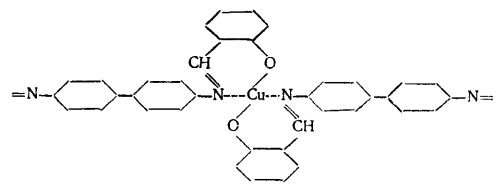
Kanda and Saito[73] have prepared high-molecular stable polychelates from 1,6-dihydroxyphenazine and Cu^{2+}, Fe^{3+}, Hg^{2+}, and Ag^{+}:



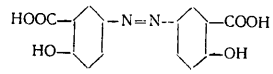
Resinous products have been obtained by reacting bis--benzoylacetone-pentamethylenediimine or bis-benzoylacetone-2,2'-diimine-diethylamine[76]:



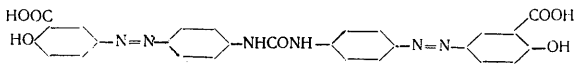
The Cu^{2+} chelates synthesised by Pfeiffer[77] from the Schiff's bases obtained from salicylaldehyde and m-phenylenediamine, p-phenylenediamine, benzidine and 1,4-diaminonaphthalene probably belong to this class of polymer. Pfeiffer gave these complexes a cyclic dimeric structure, but from their properties it may be assumed that they are polymeric[78]:



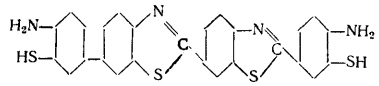
This type of polymeric chelate probably also includes the lakes formed by certain dyestuffs with metal salts, for instance:



Eriochrome Flavine A



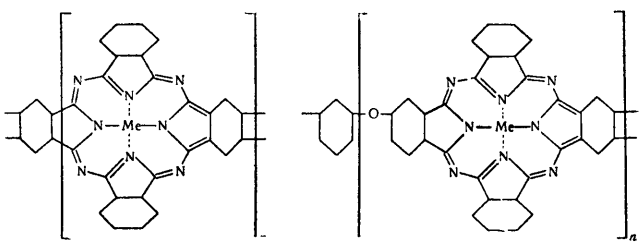
Chrysamine G



*Direct fast yellow ZKh

These lakes have not been considered from the point of view of polymer chemistry, but their structure and their ability to form complexes with salts of metals (Cr, Cu, Al, Fe) indicate that they are polymeric compounds[79].

The synthesis of polymeric phthalocyanines is of great theoretical and practical interest. The first attempts to prepare polymeric phthalocyanines from 3,3',4,4'-tetracyanodiphenyl and ions of metals of variable valency were made in 1952. Somewhat later Bailar and Drincard (cf. Marvel and Rassweiler[80]) obtained polymeric phthalocyanines from pyromellitic acid and urea, but their lack of solubility hindered the study of the polymers. In 1958 Marvel and Rassweiler[80] attempted to prepare polyphthalocyanines from pyromellitic acid, phthalic anhydride, and urea, and from 3,3',4,4' tetracarboxydiphenyl ether, phthalic anhydride, and urea:



With equimolecular properties of the reactants, linear polyphthalocyanines were obtained. The reaction mixture was heated at 170°–200° with cuprous chloride with and without ammonium molybdate as catalyst; the reaction product was a mixture of the phthalocyanine and its polymer, the presence of the catalyst decreasing the yield of polymer. The polymers are soluble in dimethylformamide and are precipitated from it by chloroform. The products are blue-green to greenish-black powders completely stable to heat, but slowly decomposing in air above 350°. They burn with difficulty, a property which leads to errors when analysing for carbon and hydrogen.

Developing the synthesis of polyphthalocyanines, Marvel and Martin[81] studied the fusion of 3,3',4,4'-tetracyanodiphenyl ether, phthalonitrile and cupric chloride in various proportions at 275° for 3 h; the products are dark blue hygroscopic powders with a metallic lustre. The sulphuric-acid solutions are brown or red-brown, as opposed to the blue sulphuric-acid solutions of copper phthalocyanine. The infra-red spectrum of these polymers shows three bands identical with those of copper phthalocyanine.

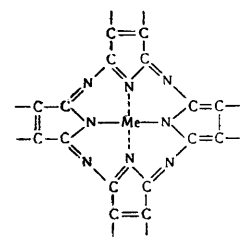
Heating a mixture of 3,3',4,4'-tetracyanodiphenyl ether with a copper salt at 275° for 3 h gives a product of very low viscosity. Increasing the reaction time leads to the formation of a three-dimensional product insoluble in sulphuric acid.

The condensation products of phthalonitrile with 3,3',4,4'-tetracyanodiphenyl ether, which are soluble in sulphuric acid, are converted into insoluble products by fusion with *p*-phenylenediamine.

All the polymeric phthalocyanines prepared by these workers decompose at 350° in air within 24 h.

Recently Berlin, Matveeva, and Sherle[82] discovered a new type of polymeric chelate, consisting mainly of carbon, nitrogen, and metal, prepared from tetracyanoethylene and metals or their compounds. On reacting 1 mole of copper acetylacetonate with 2 moles of tetracyanoethylene in a vacuum at temperatures of 160° to 300°, complex formation takes place with the liberation of acetylacetone. The product is an infusible black polymer, insoluble in organic solvents, alkalis, and dilute acids, and not decomposed by the latter.

The infra-red spectrum of a sample of the polymer did not show any intense absorption bands in the region 700–3000 cm^{-1}, except for a band at 2224 cm^{-1} corresponding to the CN group. The absence of absorption bands in this region is apparently due to the formation of polymers of a parquet structure,



Samples of the polymer show broad electron-paramagnetic-resonance lines of high intensity, with a distance between the maxima of 500–700 oersted.

The reaction of an equimolecular mixture of copper acetylacetonate, tetracyanoethylene, and phthalonitrile forms a copolymeric complex, probably of ribbon structure.

Berlin and Matveeva[83] have prepared polymeric chelates from newly synthesised polyaminoquinones. The reaction of polybenzidinodichloroquinone, prepared by condensing equimolecular quantities of chloraniline and benzidine in the presence of sodium acetate, with salts of metals (Cu, Fe, Cd, Mg, etc.) gives polymers containing 6–15% of the metal. The copper-containing polymer gives a narrow signal in its electron-paramagnetic-resonance spectrum with the *g*-factor of a free electron without hyperfine structure. In addition to the narrow signal, there is a broad symmetrical line with strong absorption in zero field. The samples of the complex possess a high magnetic susceptibility: $\kappa = 3.4 \times \times 10^{-6}$ cgs units.

This review shows that the existing data are insufficient to give a complete description of the mechanism of formation or the physico-mechanical properties of these polymers; nevertheless their structural features and the unlimited possibilities for the synthesis of various types of

* This may be better known as Immedial Yellow G G (Ed. of Translation).

polymeric chelates can lead to the preparation of new materials with a wide range of properties, occupying an intermediate position between metals and non-metallic substances.

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