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CHELATE POLYMERS

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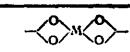
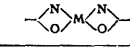
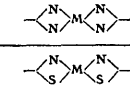
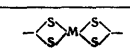
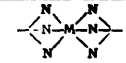
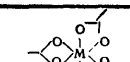
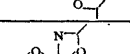
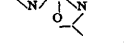
I. INTRODUCTION. SOME PROBLEMS OF TERMINOLOGY

Interest in macromolecular compounds containing metals has grown considerably during recent years. Such compounds are often termed "chelate polymers", and several reviews of work on their synthesis and properties have appeared in the Soviet and foreign literature[1-5]. Most of these, however, either do not cover the whole of the literature or else are already considerably out of date. The aim of the present review is to survey the literature on the preparation and properties of chelate polymers up to May 1962.

We must consider briefly some problems of the terminology of these compounds. The name "chelate compound" which we use is based on the term "chelate" ($\chi\eta\lambda\eta$), a claw or talon, proposed by Morgan and Drew[6]. The expressions "inner complex" and "clawlike compound" also are often employed in Soviet chemical literature. In several cases we use the nomenclature recommended by the International Union of Pure and Applied Chemistry[7].

The term "chelatophore" has been proposed[3] for a group which is capable of forming chelate rings. In our view, however, it is more appropriate to use the term "chelate ligand". Terent'ev and Rukhadze[8] proposed the name "analytical loops" for the cyclic groups formed by the addition of chelate ligands to a central atom. Later we suggested calling such cyclic chelate groups "chelate loops"[9]. The accompanying Table lists some possible chelate loops and the names and symbols which we employ for them.

Some possible chelate loops.

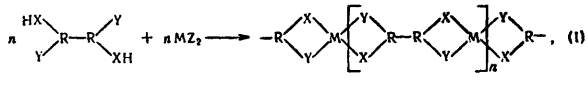
Coordination No. of metal (M)	Name of chelate	Schematic formula of chelate*	Shortened formula of chelate
4	**bisdioxa**		2(O, O) — M
4	**bisazaoxa**		2(N,O) — M
4	**bisdiaza**		2(N, N) — M
4	**bisazathia**		2(N, S) — M
4	**bisdithia**		2(S, S) — M
6	bistriaza		2(N, N, N)—M
6	trisdioxa		3(O, O) — M
6	trisazaoxa		3(N, O) — M

* In several actual cases the schematic formula can be still further simplified by representing N, O, and S atoms as points.

II. METHODS OF PREPARATION AND STRUCTURE

Chelate polymers can be synthesised in three fundamentally different ways.

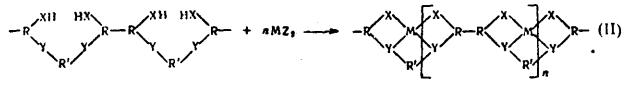
Firstly, by the metal forming donor–acceptor bonds with donor atoms in molecules which usually† contain at least two pairs of donor groups:



(I)

where X and Y are donor groups, and M is a metal.

Secondly, by entry of a metallic ion into an existing polymer chain in which the monomeric unit contains at least two pairs of donor groups:

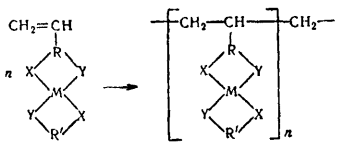


(II)

Polymers of types (I) and (II) can be formed also by the method of nascent reagents[10,11].

† In some rare cases polychelates may be formed when a chelate ligand possesses less than two pairs of donor groups, an example being provided by the hydroxo-bridged compounds. This question will be discussed in greater detail later.

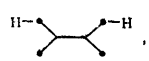
Finally, the third method of synthesis consists in the polymerisation of chelate compounds containing groups which themselves are able to undergo polymerisation:



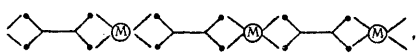
The formation of chelate polymers by the polycondensation of monomeric compounds containing chelate groups must evidently be included in this method.

The second and third methods of synthesising polychelates are usually linked with common methods for obtaining high polymers. The first method, however, is distinctive, and is applicable only to the production of coordinate-chain polymers. Such a reaction is often termed "polycoordination"[3]. Korshak *et al.*[12,13] have recently shown the similarity between the mechanism of this reaction and that of polycondensation.

Polycoordination can yield polymers with different spatial structures, both linear polychelates and planar and three-dimensional networks being possible. The structure of a given polymer is, of course, determined separately in each individual case. In particular, both the metal ion and the structure of the ligands influence the structure of a chelate polymer. In many cases the structure of the macromolecule is determined by that of the chelate loop formed. Confining ourselves to chelate polymers formed by four-coordinate metals, we can represent a bisbidentate ligand by the symbol

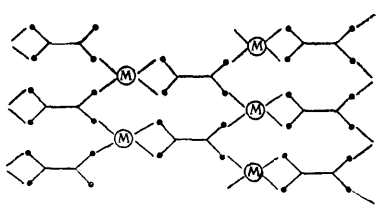


and write a linear polychelate formed by this ligand as



(III)

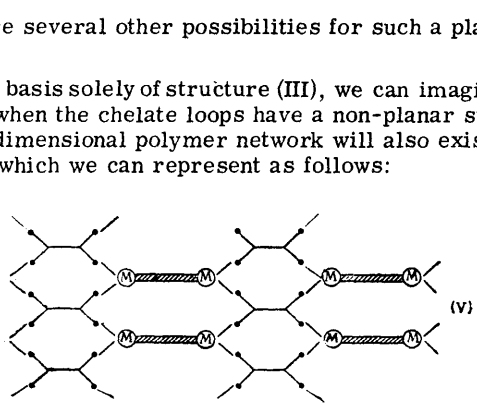
where M is a doubly charged metal ion. However, such a polymer can also have a different structure:



(IV)

There are several other possibilities for such a planar network.

On the basis solely of structure (III), we can imagine that, at least when the chelate loops have a non-planar structure, a three-dimensional polymer network will also exist, one layer of which we can represent as follows:



(V)

where ▭ denotes a ligand molecule "in profile". Here, of course, each chelate loop can form the basis of a new network layer of the polymer.

Each of the structures (III)–(V) clearly represents in some measure an "extreme case". Actually, there probably exists a definite combination of all three structures. Moreover, polychelates of any particular structure have their own rules for the building up of complete macromolecules, and it is difficult to regard chelate polymers as being completely analogous to one another. Nevertheless, in considering the various properties of polychelates it is probably necessary to start from the hypothesis that they have a network structure.

Few experimental results are available on the structure of chelate macromolecules. Terent'ev *et al.*[14,15] concluded, on the basis of a series of physicochemical properties of a large number of polychelates of differing structure, that chelate polymers are mainly two-dimensional and three-dimensional network structures. They assume that linear macromolecules are also present, although relatively few in number.

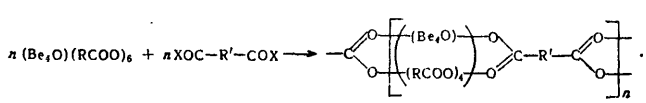
III. SYNTHESIS OF CHELATE POLYMERS

Published results show that the composition, structure, and constitution of the chelate loop have an important influence on the properties of chelate polymers. It will therefore be useful to discuss the literature on polychelates in the first place from the point of view of the composition of the chelate loop. In several cases such an approach enables the existing regularities to be revealed more clearly.

1. Polybisdioxachelates

One of the first polybisdioxachelates to be prepared was obtained in 1907 by the Russian chemists Tanator and Kurovskii[16]. In an attempt to isolate basic beryllium succinate, they obtained an infusible, transparent, vitreous product containing beryllium. Fifteen years later Meyer and Mantell[17] tried to isolate beryllium malonate, but failed to achieve satisfactory results. Neither the Russian nor the German chemists identified as polychelates the compounds which they had synthesised. A year later[18] X-ray examination of basic beryllium carboxylates showed them to be tetrahedra with the beryllium atoms at the corners and the oxygen atom in the centre, the six edges being occupied by the carboxylate groups.

Much more recently Marvel and Martin[19] established that formation of a chelate polymer required two carboxyl groups of a monobasic acid to be replaced by the carboxyl groups of a dibasic acid in the reaction

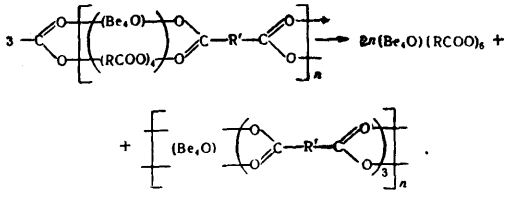


They prepared the polychelates from the basic beryllium salts of acetic, propionic, and benzoic acids, the second component of the reaction being adipoyl, sebacoyl, 3-ethyladipoyl, terephthaloyl, and isophthaloyl chlorides.

The polymers were in the form of powders, but some of them, containing only aliphatic acid radicals, could be drawn out into short filaments on plasticisation with a small quantity of solvent. Viscosity measurements showed a

very low degree of polymerisation, 4 or 5, carboxylic acid radicals obviously being located at the ends of the chains.

The polymers were thermostable right up to 350°–400°. However, even raising the temperature to only 110°–140° caused disproportionation to start, resulting in an insoluble and infusible network polychelate:



The disproportionation of beryllium carboxylates was known still earlier. Thus beryllium oxide acetate undergoes intramolecular rearrangement in boiling methanol or ethanol with the formation of the polychelate[20,21]

$$(Be_4O)(CH_3COO)_6 \rightarrow [(Be_4O_m)(CH_3COO)_{6-2m}]_n,$$

where $m = 2, 4$ and $n \gg m$. A similar transformation takes place even more rapidly at higher temperatures, for example in boiling butanol or decanol[22] and also in pyridine[23].

Marvel and Martin[19] also carried out the radical polymerisation of basic beryllium carboxylates containing acrylic acid radicals. In the presence of benzoyl peroxide, insoluble network polychelates were obtained. A network polymer was formed even when the basic beryllium carboxylate contained only one acrylate group. This phenomenon was explained in terms of the disproportionation reaction, which these workers had discovered. The polymers thus obtained already decomposed vigorously at 200°.

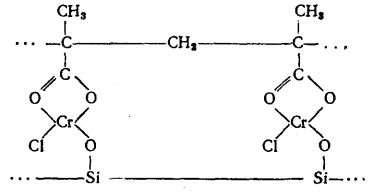
Macromolecular compounds based on acrylic acid have been known for a long time, and have been well investigated. Such polymers contain repeating carboxyl groups, which in some cases can form polychelates with various metal ions. A chelate loop of the type 2(O, O)–M is also formed. Several papers have been published on the synthesis and some of the properties of these compounds.

Wall and Gill[24] investigated the interaction of copper(II) ions with polyacrylic acid, and established from the infrared spectra and polarographic studies that a copper complex is formed: the titration curves show that each copper(II) ion replaces two hydrogen atoms to form a chelate compound. The copper polychelate differs from the compounds formed by the alkaline earth metals with polyacrylic acid, in which electrostatic interaction predominates[25]. It is interesting that nickel, zinc, and cobalt ions exhibit only a feeble tendency to form polychelates with polyacrylic acid.

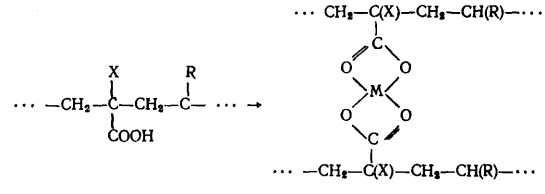
Morawetz[26] and Kotliar and Morawetz[27] investigated the tendency of copper acetate to form complexes with polyacrylic and polymethacrylic acids. From the results of titration, dialysis, and spectroscopic examination they established that each copper ion is linked with four oxygen atoms of these polymeric acids. The number of chelate loops formed depends on electrostatic factors and the concentration of the polymer. Gregor and his coworkers showed, in an examination of the complexing properties of polyacrylic acid, that the copper(II) polymers are extremely stable[28]. They remark[29] that the formation of copper polychelates is more difficult with cross-linked polyacrylic and polymethacrylic acids (1–9% of divinylbenzene in the copolymer) than with the linear polymers. Alkaline earth metals form[30] far less stable chelate polymers than does copper(II). After copper, the manganese and zinc polychelates were the most stable.

The barium salt of isotactic polyacrylic acid of molecular weight 60 000 has been described recently[31]. The electron micrographs indicate that the macromolecules have a compact globular structure, and remain unchanged over the pH range 4.2–10.7. Consolidation of the initial ball of isotactic polyacrylic acid is associated with the formation of stable bonds between the barium counterions and the carboxyl groups of the acid.

A noteworthy du Pont patent[32] reports the preparation of a polychelate of chromium with polyacrylic acid of low molecular weight on an ordinary silicate glass surface. In this case the chromium ion probably forms a link between the silicon atoms in the glass and the organic polymer:

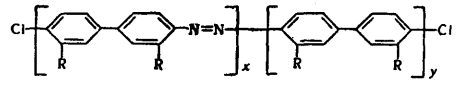


Interesting work has also been done on the synthesis of polychelates based on polymers and copolymers of several other unsaturated acids with metals. The possibility of the formation and industrial application of polymers of this type was noted by Berlin[33] as early as 1947. Copolymers of unsaturated acids with some unsaturated monomers contain systems of carboxyl groups. When such copolymers are compressed with salts or oxides of metals at 120°–140°, it is possible to obtain insoluble, heat-resistant, three-dimensional polychelates:



Morawetz *et al.*[34] prepared chelate polymers of alkaline earth metals with hydrolysed copolymers of maleic anhydride with styrene and ethyl vinyl ether.

The preparation and properties of some aromatic polymers having a conjugated bond system have been described more recently by Berlin *et al.*[35] Compounds of general structure



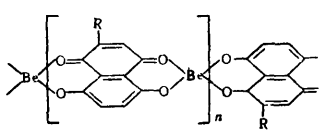
where R = H or COOH, were obtained by the decomposition of bisdiazotised derivatives of benzidine and of benzidine-3,3′-dicarboxylic acid. The macromolecular compound obtained from the acid was found to react with copper salts to form a three-dimensional chelate polymer, as was confirmed by the electron paramagnetic resonance spectra of this compound.

Compounds formed by reaction of various metal derivatives with bis-β-diketones represent a large and distinctive group of chelate polymers. The peculiarity of this

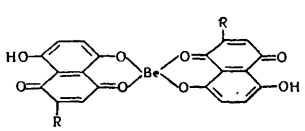
group is that the metal atoms form part of the main chain of the polymer, and have a substantial influence on the properties of the resulting macromolecular compounds.

Among the first workers to obtain chelate polymers based on bis-β-diketones were Bailes and Calvin[36], who, in a research on compounds which might act as artificial oxygen-carriers, turned to some peculiar compounds of cobalt. Among the huge number of substances which they examined, two were chelate polymers having the structure 2(O, O)–Co. The starting materials for the synthesis of such polymers were 4,6-dihydroxybenzene-1,3-dialdehyde and naphthazarin respectively. The products were yellow powders, which on being heated each lost two molecules of water of crystallisation per chain unit.

Underwood and his collaborators suggested naphthazarin and alkannin as reagents for the colorimetric determination of beryllium[37,38], the compounds thus formed obviously being chelate polymers. However, the composition of the products could not be established. A separate investigation showed that beryllium reacts with naphthazarin and alkannin to form two pairs of complexes depending on the proportions of the starting materials[39]. These workers consider that, when the ratio of beryllium to naphthazarin is 1 : 1, the product is a polychelate of the structure



where R represents H in the case of naphthazarin, and $-CH(OH).CH_2.CH:C(CH_3)_2$ in the case of alkannin. When the ratio of beryllium salt to ligand is 1 : 2, the product has the constitution

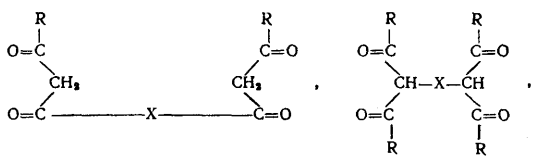


Still earlier a polymer of quinizarin with copper had probably been obtained by Flumiani and Bajić[40,41], but they did not identify their product as polymeric.

In 1953 Wilkins and Wittbecker patented[42] the preparation of chelate polymers by the reaction of various bis-β-diketones with acetylacetonates of bivalent metals. The bis-β-diketones used were terephthaloyldiacetone, bis-*p*-acetoacetylphenyl ether, 1,8-bisbenzoylacetyloctane, and *p*-bis-2,2-diacetylethylbenzene. Polychelates were obtained with the following four-coordinate bivalent metals: Be, Cu, Ni, Zn, Co, Fe, Pd, Mn, Ca, Sr, Ba, and Cd. The reaction was carried out by heating a mixture of the metal acetylacetonate and the bis-β-diketone in a vacuum, the acetylacetone distilling off. The patentees varied the reaction conditions, the metal ions, and the tetraketones, and prepared polymers suitable for the production of coatings, moulded articles, filaments, and films.

Glukhov[43] reported the preparation of a series of chelate polymers of Be, Mg, Ca, Zn, Cu, Co, and Fe with various bis-β-diketone derivatives of acetylacetone. He found that the polybisdioxachelates of beryllium were the most stable to heat, for they decomposed only at 350°. Polychelates were prepared[44] by emulsion polymerisation of the tetraketones and water-soluble salts of the above metals in aqueous chloroform at 40°–60° for 2 h. The products were powders: white in the cases of Be, Mg, and Ca, dark blue with Cu, green with Fe, and red with Co. The chelate polymers were soluble in pyridine and in dimethylformamide, with $[\eta] \simeq 0.1$. In this series of tetraketones, too, the beryllium polychelates were the most stable to heat.

During the past three years, Korshak and his coworkers have published a series of papers[12,13,45–54] on the synthesis and properties of the chelate polymers of metals with various tetraketones. A series of polychelates was described, formed by bivalent metals (Be, Cu, Ni, Zn, Co, Cd, and Mn) with bis-β-diketones having the structure



where X = $[CH_2]_3$, $(CH_2)_6$, $C_6H_4.CH_2.C_6H_4$, *p*-C_6H_4, *m*-C_6H_4, *p*-$C_6H_4.C_6H_4$-*p*′, $CH_2.C_6H_4.C_6H_4.CH_2$, $C_6H_4.O.C_6H_4$, etc., and R = CH_3, C_6H_5, OH, OCH_3.

The overwhelming majority of chelate polymers have been obtained as coloured amorphous powders, sparingly soluble or else completely insoluble in the usual organic solvents. The beryllium compounds are more soluble than others.

The thermal stability of the polychelates increases with increase in the number of phenyl groups in the initial tetraketone. The thermal properties of the polymers also depend on the metal ion, the stability diminishing in the sequence: Cu > Be > Ni > Co > Zn > Mn > Cd. Degradation of the polymers starts at 250°–400° with the various specimens.

Molecular weights were determined ebullioscopically in chloroform in the case of soluble polymers, and by approximate calculation from analytical results in the case of insoluble compounds. From these calculations the degree of polymerisation did not exceed 25, and had a value of 52 only for the chelate polymer of copper with *pp*′-diacetoacetylbiphenyl.

More recently, Korshak and Vinogradova[12,54] have reported the osmometric determination of the molecular weight of the polychelate formed by beryllium with *pp*′-bisacetoacetylphenyl ether; one of the chloroform-soluble fractions of this polymer had a molecular weight of 126 000.

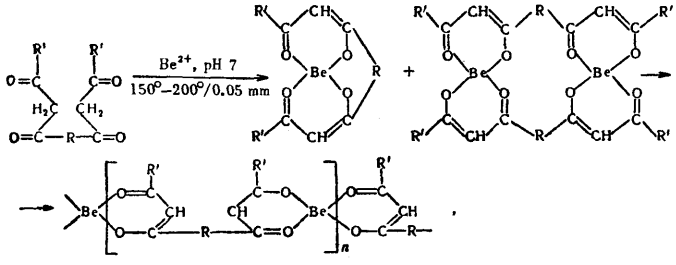
It has also been shown[48] that the thermal stability of chelate polymers based on bis-β-diketones is more clearly linked with the flexibility of the macromolecular chain than with solubility. X-Ray examination established[46] that a decrease in molecular weight is accompanied by an increased degree of order in the molecular structure.

Chelate polymers have also been obtained of the bivalent metals Cu, Ni, Zn, Co, Cd, and Mn with quinizarin[46]. They are infusible coloured powders which are stable up to 350°–400°.

A noteworthy paper by Knobloch and Rauscher[55] describes the original use of interfacial polycondensation for the preparation of chelate polymers, the components being 3-hydroxy-2-enones (tetraacetylethane and quinizarin), which are soluble in benzene or in ethylene dichloride, and aqueous cuprammonium solution. These workers emphasise that such interfacial polycondensation can be accomplished only if the copper is present as an unstable complex in the aqueous solution. Polychelates are still formed when the ammonia is replaced by pyridine, but the bis-ethylenediamine and glycine complexes of copper no longer give chelate polymers. Similar results were obtained with nickel(II) ions.

In order to produce thermostable plastics, Kenney[56] prepared polybisdioxachelates of Be, Cu, Ni, Zn, Co, and Fe and polytrisdioxachelates of Al. The polymers were synthesised by fusing the corresponding metal acetylacetonates with the bis-β-diketone in a vacuum, when several of the resulting compounds could be isolated as brittle films. The molecular weight of these compounds did not exceed 4000. On being heated in air at 300° for 3 h, the chelate polymers lost 16–46% of their weight.

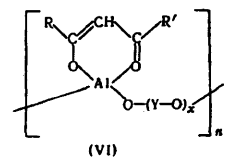
Kluiber and Lewis[57] prepared macromolecular chelate compounds with various bis-β-diketones according to the scheme



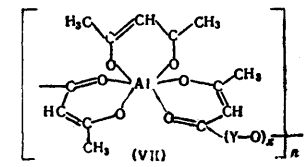
the intermediate products being isolated and characterised. They regard this as a new method for synthesising polychelates. In fact, this is the first work to show the possibility of formation of a macromolecular complex by ring cleavage. However, the authors themselves comment that aliphatic bis-β-diketones were used in which R = $[CH_2]_x$ (x = 6–12), and rearrangement of the macrocyclic rings into polychelates was found to take place more readily the longer the carbon chain (*i.e.* the higher the value of x). The presence of aromatic or conjugated systems in the macrocycle will obviously modify the rearrangement, or even lead to the direct formation of a polychelate. Kluiber and Lewis also consider, on the basis of viscosity measurements in benzene and of fluidities at moderate temperatures, that the final products have a high molecular weight. This hypothesis is supported also by the amorphous character of such compounds, as shown by the X-ray powder diagrams.

An interesting paper by Kugler[58] on the preparation of chelate polymers of aluminium shows that reaction between aluminium alkoxides and acetoacetic ester yields a compound in which a keto-ester grouping is combined with the aluminium atom in a chelate ring. On hydrolysis, such systems split off ethyl alcohol, and at high temperatures rearrangement takes place, with loss of water and formation of a polychelate.

Two years later Patterson *et al.*[59] described a series of chelate polymers of aluminium similar in structure to those obtained by Kugler[58]. They investigated the properties of polycondensates containing aluminium atoms in the chain, and attempted to increase the stability of such compounds by linking the aluminium in a chelate ring. Polymers of two types of structure were obtained



(VI)



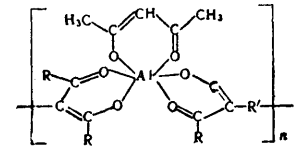
(VII)

where normally R = R′ = CH_3 and Y is the radical of the diols HO.Y.OH. Polychelates having the structure (VI) are unstable to hydrolysis. They have low melting points, are soluble, and are thermally unstable. On being heated, however, they can disproportionate to give thermally stable, infusible, network polymers.

Chelate polymers having the structure (VII) are infusible powders, stable up to 360°. Their molecular weights were determined cryoscopically in benzene, in which several of the polymers were soluble, and lie within the range 400–2620.

The diols used were mono-, di-, and tri-ethylene glycols, butane-1,3(and 1,4)-diols, and also pentane-1,5--diol. An especially interesting diol was 2,2-diphenylpropane-*pp*′-diol, the polychelate of which was soluble in methanol. From it could be isolated hard, brittle, transparent, colourless films which were stable in air.

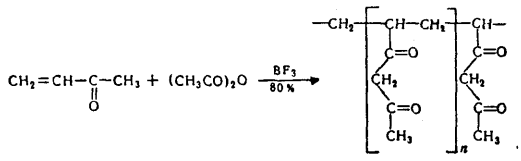
The polycondensation polymers thus obtained should have a linear structure. In order to obtain polychelates having a different spatial arrangement of the macromolecular chains, these workers turned to tetraketones, and synthesised more than a hundred chelate polymers of aluminium having the general formula:



where R = CH_3, C_6H_5, or OC_2H_5; R′ = C_6H_4 or $[CH_2]_x$, with x = 0–5. It is seen from the formula that four coordination positions in these compounds are occupied by the oxygen atoms of the tetraketones, and two by the acetylacetone grouping. These compounds were infusible and stable to heat, and probably represent polymers having a three--dimensional network structure.

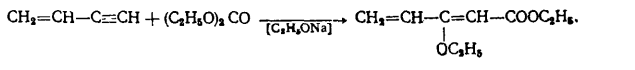
Formation of a network polymer can be expected also when the β-diketone radical forms part of the monomer unit of a carbon-chain or heterochain polymer. At the same time, formation of a network polymer in the synthesis of a polychelate having this type of structure makes it difficult to coordinate the metal ions with all the β-diketone groupings.

The preparation of chelate polymers in this way has been described by Hoeschele *et al.*[60], who were able to synthesise polyacetoacetylethylene by the ionic polymerisation of methyl vinyl ketone in acetic anhydride:

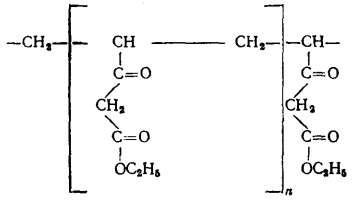


Comparison of the stability of these polychelates with that of the corresponding acetylacetonate complexes showed approximate equality in the copper, neodymium, and praseodymium chelate compounds, while the uranyl chelate polymer was about three times as stable as the corresponding acetylacetonate.

Cairns *et al.*[61] described the synthesis of ethyl 3-ethoxypenta-2,4-dienoate from but-1-en-3-yne:



The resulting compound readily polymerises both on standing in air and under the influence of compounds containing oxygen or nitrogen. The polymer thus formed can be hydrolysed to the corresponding keto-ester:



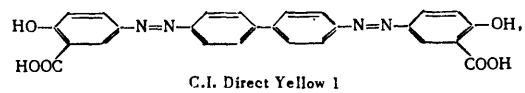
The latter can in turn yield chelate polymers. These workers described a copper polychelate of this type in which, from the analytical results, copper appeared to have entered 23% of the keto-ester groupings. This substance was an infusible and non-softening dark green powder, most probably a network polymer.

In 1958 a du Pont patent[62] claimed the production of solutions for the preparation of insoluble, hard polymeric coatings. On evaporation of the solvent, polychelates were formed of beryllium, aluminium, and other metals with various polymeric chelate ligands. The latter could include poly(allyl acetoacetate), copolymers of vinyl acetate and salicylaldehyde and of styrene and acryloylacetone, and other polymers and copolymers having donor atoms.

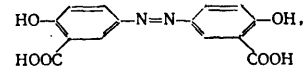
Several bis-*o*-hydroxycarboxylic and bis-*o*-dicarboxylic acids, as well as bis-β-diketones, are able to form polybisdioxachelates. Thus chelate polymers have been obtained from bivalent beryllium and iron with tetrasalicoylferrocene[63]. The electrical conductivity of such polychelates[64] is several orders of magnitude greater than that of the usual organic dielectrics, and approaches the conductivity of some organic semiconductors[65,66].

Terent'ev *et al.* have described[67] the synthesis and properties of polychelates of copper, nickel, iron, and cobalt with methylene-5,5'-bissalicylaldehyde, the products all being coloured amorphous powders of network structure. Magnetochemical measurements showed the chelate loops of all the polymers to have a tetrahedral structure.

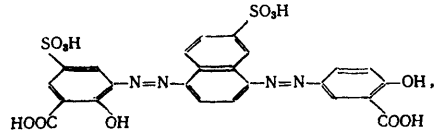
Several lakes formed by the interaction of a series of dyes and metal salts are regarded by Berlin and Matveeva[3] as chelate polymers. For example, the following three compounds



C.I. Direct Yellow 1



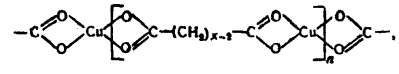
C.I. Mordant Yellow 5



C.I. Mordant Brown 51

give stable chelate compounds with salts of copper, chromium, aluminium, and iron[68]. From the structure of such dyes it must be assumed that their metal complexes are polymers.

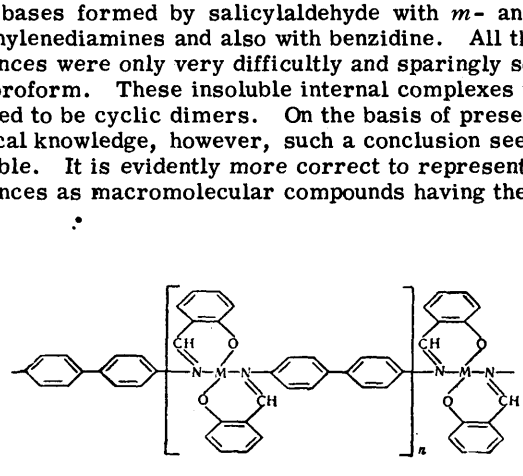
Interesting work has also been done by Kubo *et al.*[69] on the structure of the chelate polymers formed by copper with various dicarboxylic acids, their general formula being



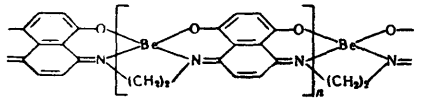
where $x = 2-10$. From measurements of magnetic moments they conclude that a network structure is most probable for $\alpha\omega$-dicarboxylic acids having an even number of carbon atoms. This conclusion is supported by results for infrared spectra, especially the C=O stretching vibrations and the rotational oscillations of the CH_2 groups.

2. Polybisazaoxachelates

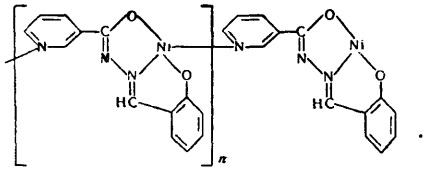
Among the earliest investigators to obtain polybisazaoxachelates were Pfeiffer and Pfitzner[70], who as long ago as 1936 described the preparation of copper complexes of Schiff bases formed by salicylaldehyde with *m*- and *p*-phenylenediamines and also with benzidine. All these substances were only very difficultly and sparingly soluble in chloroform. These insoluble internal complexes were assumed to be cyclic dimers. On the basis of present-day chemical knowledge, however, such a conclusion seems debatable. It is evidently more correct to represent these substances as macromolecular compounds having the structure:



Dubsky *et al.*[71] investigated the products formed by solutions of beryllium salts with naphthazarin in the presence of ethylenediamine, and found that the latter two compounds interact, forming a ketimine compound with the beryllium. It can be assumed that the products were chelate polymers

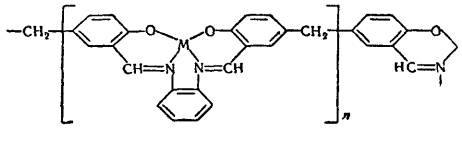


Sacconi[72] prepared Schiff bases from pyridine-3-carbohydrazide and salicylaldehyde, 5-bromosalicylaldehyde, *o*-hydroxyacetophenone, and *o*-hydroxynaphthaldehyde. These compounds reacted with nickel acetate to form amorphous substances, insoluble in water and in organic solvents, having the polymeric structure:



All the compounds were stable up to 350°, and possessed remarkable chemical resistance.

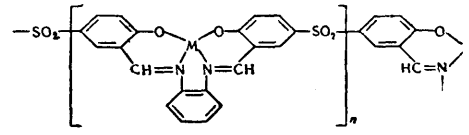
Marvel and Tarköy[73] prepared and examined the thermal stability of the chelate polymers of bivalent Cu, Ni, Zn, Fe, Co, and Cd with Schiff bases formed from methylene-5,5′--bissalicylaldehyde and *o*-phenylenediamine. A polymeric Schiff base was isolated which was an orange substance soluble in tetrahydrofuran. The viscosity of this compound indicated its degree of polymerisation to be 45. On treatment of this polymer in air with solutions of metal acetates at room temperature for 6 days, polychelates



were isolated as infusible coloured powders, which were also regarded as having a degree of polymerisation of 45. They showed considerable thermal stability: on being heated in air at 250° for 3 h, the losses in weight were 11–26%.

Somewhat later Terent'ev and his coworkers[9,74] prepared chelate polymers of Cu, Ni, Zn, Fe, Co, and Cd with Schiff bases formed by methylene-5,5′-bissalicylaldehyde with ammonia, ethylenediamine, hexamethylenediamine, and *o*-phenylenediamine. Polychelates of this type can readily be synthesised by the nascent reagent method. A comparative magnetochemical study of the products showed several structural regularities in the chelate loops of such polymers. It has also been established[14] that all the polychelates are amorphous substances having an appreciable predominance of network structures. Some of the compounds synthesised had semiconducting properties[75], and others found application in the rubber industry[15].

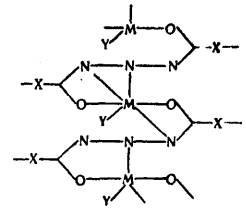
Marvel and Tarköy[76] also synthesised chelate polymers of the same metals with Schiff bases of sulphonyl-5,5′-bissalicylaldehyde and *o*-phenylenediamine



the products being infusible, insoluble, and coloured. The nickel and cadmium compounds were thermally the most stable.

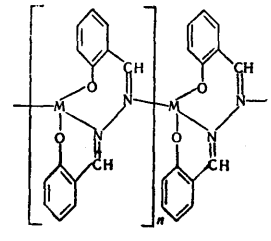
Spitsyn and his coworkers[77] reached the same conclusions from an examination of the properties of chlorinated and brominated polychelates of similar structure.

Goodwin and Bailar[78] obtained thermally stable polymers containing cobalt, aluminium, and chromium, using as chelate ligands polymeric Schiff bases formed from methylene-5,5′-bissalicylaldehyde and sulphonyl-5,5′-bissalicylaldehyde with diethylenetriamine. They assume that substances of the following structure are formed:



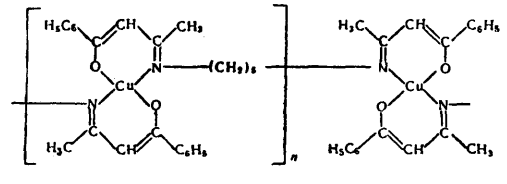
where X = $CH_2.CH_2$, SO_2; M = Co^{3+}, Al^{3+}, Cr^{3+}; and Y = Cl^-, NO_3^-, $\frac{1}{2}SO_4^{2-}$.

Marvel and Bonsignore[79] obtained macromolecular chelate compounds

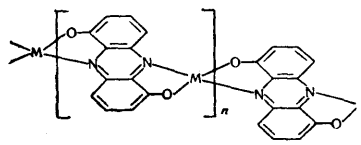


by the reaction of salicylideneazine with salts of copper, nickel, zinc, cobalt, and cadmium. The polymeric structure of such compounds is suggested by their insolubility in water and organic solvents, and also by their appreciable thermal stability.

Several Schiff bases of 1-phenylbutane-1,3-dione give resins and rubberlike products with copper acetate[80], this being explained by the formation of chelate polymers having the structure

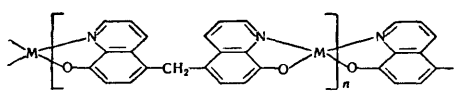


Another good compound for complex formation was phenazine-1,6-diol, which yielded polychelates



with Cu^{2+}, Fe^{3+}, Hg^{2+}, and other metals [81].

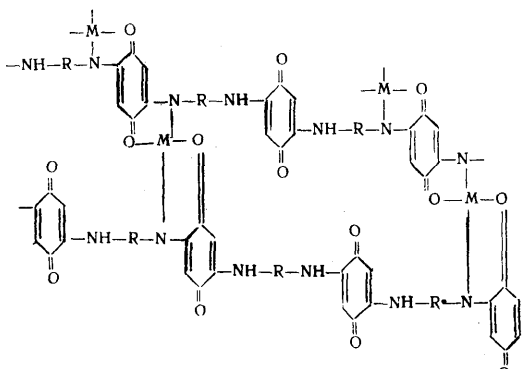
Korshak *et al.* [82] described polychelates of methylene--5,5′-bisquinoline-8,8′-diol with metals. Reaction of this compound with the acetylacetonates of Cu, Ni, Zn, Co, Cd, and Mn gave chelate polymers of molecular weight not exceeding 9000



These workers also obtained interesting unsymmetrical polychelates, using either two different chelate ligands with the same metal or two metals with the same chelate ligand. Besides the above quinoline derivative, quinizarin was also used as ligand. The unsymmetrical coordination compounds were found to have similar properties to those of the homogeneous polychelates. All these compounds were coloured powders. The thermomechanical curves indicate that the polymers undergo degradation at 250°–400°.

The work on polybisazaoxachelates of Berlin and his collaborators is also of great interest. Reaction of a chloramine with benzidine and some other diamines enabled these workers to obtain infusible, almost black polymers which were insoluble in the usual organic solvents [83–85]. These compounds were soluble in concentrated sulphuric acid and partly soluble in formic acid and dimethylformamide. End-group determinations showed their molecular weight to be 2000.

The presence in polyaminoquinones of *ortho* C=O and NH groups made it possible to obtain a series of chelate polymers of copper, magnesium, cadmium, and other metals of general structure

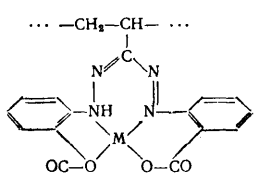


The low metal content (6–12%) compared with the theoretical indicates that cross-linking involves some of the C=O and NH groups. This hypothesis is supported also by the presence of a hydrogen bond, revealed by the infrared spectrum.

The electron paramagnetic resonance spectra of the synthesised polyaminoquinones contained asymmetric lines, although the latter appeared only when the molecular weight of the polymer had become fairly high. The concentration of unpaired electrons in these cases was 10^{20}–10^{21} g^{-1}. When the temperature was lowered to 80°K, the electron paramagnetic resonance absorption disappeared, recalling the behaviour of paramagnetics having antiferromagnetic properties. The corresponding chelate polymers of copper exhibited an electron paramagnetic resonance spectrum practically identical with that of the original highly polymerised metal-free compound. It is interesting that the entry of copper not only intensifies the signal but also preserves it down to the temperatures of liquid nitrogen. The above workers suggest, however, that this phenomenon is due to further cross-linking, not with the presence of actual unpaired *d* electrons on the metal ions.

Several investigators have obtained polybisazaoxachelates by introducing chelate groups into a carbon-chain polymer. Thus Maynard [86] treated a 47% solution of a 10 : 2 : 1.1 butadiene–methacrylonitrile–styrene copolymer in decalin with ethylene glycol, and then aminated the resulting mixture with ammonia. He treated the polyamine thus obtained, containing about 10% of total nitrogen and 2.5% of amine nitrogen, with salicylaldehyde in benzene solution, distilled off 5 parts of the condensed water, and treated the resulting rubberlike product with metal salts, obtaining insoluble polychelates with the ions Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}, Hg^{+}, Sn^{2+}, and Sn^{4+}.

Interesting polychelates were obtained by Schulz [87], who found that polypropenal can react with the usual reagents for aldehydes, forming oximes, hydrazones, and phenylhydrazones. *o*-Hydrazinobenzoic acid yields a poly(propenal *o*-carboxyphenylhydrazone) containing 70 mole % of hydrazone groups, which with diazotised anthranilic acid forms a polymeric formazan more readily. Like the formazans of low molecular weight, this polymer forms very stable metal complexes, for example with Cu^{2+} and UO_2^{2+}, but not with Ni^{2+} or Mn^{2+}.

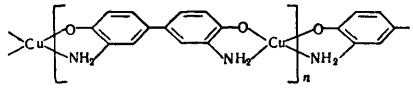


Schulz correctly assumes that this property of the polymers can be utilised in the construction of columns for the selective separation of these ions.

Polybisazaoxachelates have attracted the attention of many American research workers. Apart from the papers mentioned above, several technical reports on the synthesis and properties of chelate polymers have been published in the USA. This work has been carried out in Ohio under the direction of well-known specialists in the field of coordination compounds (Bailar, Fernelius, and others) [88,89]. However, we have no knowledge of the exact contents of these reports‡. It is noteworthy that it is in Ohio, which contains one of the scientific research centres of the United States Air Force, that the principal American investigations on the properties of chelate polymers have been carried out, the main purpose being to find new thermostable materials. Characteristically, properties of polychelates other than their thermal properties have been studied

‡ Copies of these reports are not held by the Lenin State Library, in the Library of Foreign Literature.

extremely superficially in this work. Nevertheless, several papers and lectures by various American scientists give some information on the polychelates which have been investigated in Ohio. Thus Shaw[5] reported in particular that a polychelate of the structure

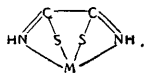


had been synthesised and studied in Ohio, but he did not give the properties of this compound.

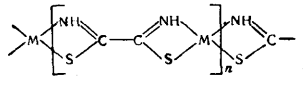
Atlas and Mark[4] have more recently written a brief survey of thermostable polymers. On the basis of information presented at the Conference on High-Temperature Polymers held in May 1959 at Dayton (USA) they give structures for a few new polybisazaoxachelates synthesised in Ohio by Bailar, who obtained a series of chelate polymers by fusing biquinolyl-8,8′-diol with zinc, copper, and nickel salts. Other chelate ligands used included bisdiphenols, bissalicylic acids, and derivatives of *o*-aminophenols. All the substances obtained were thermostable coloured powders.

3. Polybisazathiachelates

Possibly the most interesting polymers having the chelate loop 2(N, S)–M are the compounds formed by metals with rubeanic acid, for which as early as 1926 Rây and Rây[90] proposed the following structural formula:

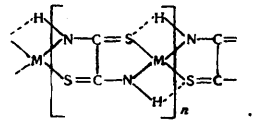


This formula was regarded as correct until 1944, when Jensen[91] concluded from an investigation of the chemical properties of a series of internal complexes that the salts of rubeanic acid are polymers having the structure



He also showed that the old formulae for these salts were impossible owing to steric hindrance.

Almost fifteen years later Piper[92] suggested a formula for metal polyrubeanates with repeating five-membered rings in the *trans* form, based on spectroscopic and magnetochemical data. Almost simultaneously a paper by Barcelo[93] reported similar conclusions based on infrared spectra, and proposed the following formula for polyrubeanates:

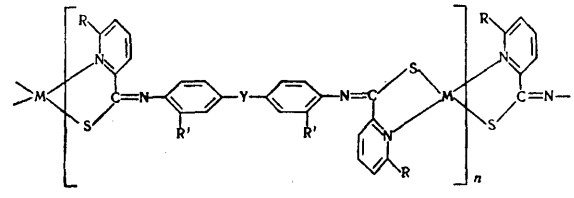


There are indications in the literature[94], however, that the polymer may exist in the *cis* form. Kubo *et al.*[69] assume further that copper polyrubeanate (other metals were not investigated) is a planar network, not a linear structure. This view is based on the low magnetic moments of copper polychelates.

Quite recently[95] polychelates of nickel with *NN′*-disubstituted dithiooxamides have been obtained (the tetrasubstituted compound does not form a polychelate). All these chelate polymers are amorphous powders, insoluble in solvents. They are stable on being heated to 300°–400°. *NN′*-Diacetoxydithiooxamide gives with nickel a polychelate which is soluble in several hot mineral oils and nitrobenzene. Such properties are probably associated with the relatively low molecular weight of this compound. The nickel poly-*NN′*-dimethyldithiooxamide derivative also probably possesses a low degree of polymerisation. It is crystalline and decomposes at a lower temperature. Measurement of the magnetic susceptibility of the polychelates showed that in several cases the magnetic moment was 2.4 μ_B, which is attributed to the simultaneous presence in the macromolecule of chelate loops with both planar and tetrahedral configurations, with the latter predominating.

Polyrubeanates have also found practical application. For example, the preparation of a molecularly oriented polymeric plastic which polarises light has been patented[96], the polymer containing nickel and copper polydithiooxamides as additives. The semiconducting properties of polyrubeanates have also been described[75].

Polybisazathiachelates of general formula



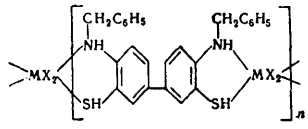
(VIII)

(where R = R′ = H, and Y = SO_2, O, CO, or is absent altogether) were obtained by Martin[97] by the interaction of 2-methylpyridine, sulphur, and various diamines. These substances, while possessing two pairs of donor groups, readily undergo polycoordination with the four-coordinate bivalent ions of copper, nickel, zinc, and mercury. He was unable to determine any end-group from the infrared spectra. Elementary analysis also suggests that the polymer chain is of indeterminate length. Martin assumes that his synthetic polychelates have molecular weights of about 15 000. Thermal stabilities of the polymers were determined on a thermogravimetric balance. Vigorous decomposition starts at 340°–400°. The zinc compounds show the greatest thermal stability, which is in turn affected by the nature of the group Y. Maximum thermal stability is achieved when Y = SO_2. Thus the various polychelates of zinc decompose above 400°, but when Y = SO_2 the polymer is so stable that its infrared spectrum shows no change in structure after heating in air at this temperature for 6 h. Introduction of the bridging groups Y = O and CO into the original molecule does not lead to the production of plastic polychelates.

Terent'ev *et al.*[98] also investigated the properties of chelate polymers having the structure (VIII) with R = H or CH_3, R′ = H or OCH_3, and Y absent. It was found that introduction of methoxy-groups increases the solubility of

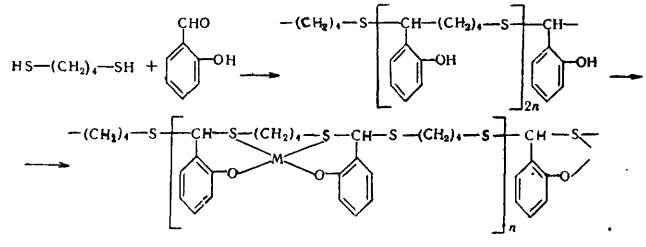
the compounds, while their molecular weights do not exceed 40 000–45 000. Magnetochemical examination showed that the polymers had chelate loops of tetrahedral structure.

Eirich and Mark[99] have reported the preparation of a chelate polymer having the structure



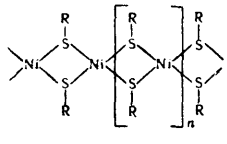
where X represents Cl^- or other substituent attached to the metal. The polychelate was synthesised by the interaction of toluene, benzidine, and sulphur, followed by treatment with a salt of the metal. However, the above formula seems extremely doubtful to us. The hydrogen of the thiol group is sufficiently acidic to be replaced by a metal. It can only be supposed that, since this work was merely reported at a conference, it contained some unverified results.

Atlas and Mark[4], at the Conference on High-Temperature Polymers held in Dayton in May 1959, mention that Drinkard (University of California) has described the reaction between alkanedithiols and aldehydes, leading to the formation of polymeric mercaptals. If any coordinate groups still remain in such a molecule, chelate polymers can be formed. The following reaction is cited as an example

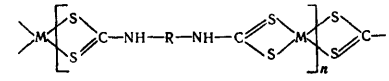


4. Polybisdithiachelates

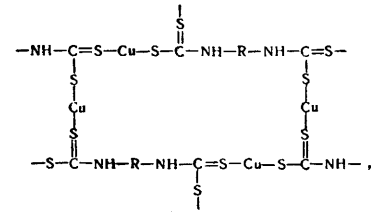
The first investigator to obtain polybisdithiachelates was probably Jensen[91]. While studying the mercaptides of nickel, he turned his attention to the extraordinarily close similarity in properties between the nickel compounds of benzoquinoline-8-thiol and of 2-methylquinoline-4-thiol. The former compound, unlike the latter, can yield a non-polymeric internal complex. From a comparison of the colour, solubility, and magnetic properties of benzoquinolinethiols, benzothiazole-2-thiol, and several other thiol derivatives, he concluded that these compounds contain a planar chelate loop with four-coordinate bivalent nickel having the structure 2(S, S)–Ni. Jensen hence decided that nickel mercaptides are highly polymerised compounds of the type



For a long time after this no one took an interest in polybisdithiachelates. It is only recently that a few papers by Terent'ev and his coworkers have appeared describing the synthesis[100] and properties[75,101,102] of chelate polymers containing the chelate loop 2(S, S)–M. These are compounds formed by several metals with biscarbamodithioic acids, and have the general formula



where R = $[CH_2]_2$, $[CH_2]_3$, p-C_6H_4, p-$C_6H_4.C_6H_4$-p'; M = Ni^{2+}, Zn^{2+}, Co^{2+}. Polychelates having this structure were obtained by the reaction of aqueous solutions of the corresponding sodium biscarbamodithioates with the metal acetates. These workers were able to show[100] that, in the case of copper(II) salts, such reaction is accompanied by reduction of the latter to copper(I) with simultaneous formation of a polymer having a two-dimensional network structure



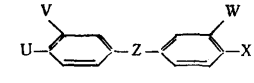
where R has the same significance.

Polybisdithiachelates are fine powders of various colours. They are extremely difficultly soluble and are infusible. The chelate polymers are thermostable, decomposing above 350°. They most probably possess a network structure. Their electrical properties are especially interesting[75]; several substances have been found to possess semiconductor characteristics. These same polybisdithiachelates proved to be strong catalysts for the decomposition of hydrazine[102].

5. Polybisdiazachelates

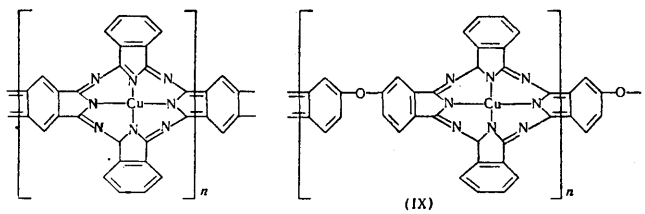
Polybisdiazachelates form a distinctive group of chelate polymers. They include firstly polymers which to a certain extent repeat the structure of such important and interesting compounds as the phthalocyanines, haemin, and chlorophyll.

As early as 1949 Ciba Ltd. patented[103,104] the preparation of polymeric phthalocyanines having a relatively low degree of polymerisation. A phthalocyanine dye is obtained by reaction of the substance



(in which Z is the radical of a simple dibasic acid, for example carbonic or sulphuric acid, and U, V, W, and X represent CO or CN groups) with copper halides and dicyanoaryls or o-dicarboxylic acids in the presence of urea. Ammonium molybdate is used as catalyst. The product is a black powder, practically insoluble in organic solvents, but dissolving in concentrated sulphuric acid to form a green solution.

Since copper phthalocyanine possesses high thermal stability and can be sublimed in a current of nitrogen at 560° without decomposition, it and its analogues have attracted the attention of chemists not only as excellent dyes but also as possible polymers of astonishing thermal stability. Marvel and Rassweiler[105] obtained polymeric phthalocyanines by the interaction of pyromellitic acid, phthalic anhydride, and urea, and also from the 3,3′,4,4′--tetracarboxylic acid of diphenyl ether, phthalic anhydride, and urea. The metal ion used was copper(II). The infrared spectra of the resulting polymers showed that their structure was in fact similar to that of phthalocyanine:



(IX)

however, they were of low molecular weight.

This paper gives references to some American work done under contract in 1952 and 1956, which also had the purpose of obtaining polymeric phthalocyanines. Thus in 1956 Bailar and Drinkard prepared a phthalocyanine-like polymer from pyromellitic acid and urea, but the product was insoluble and could not be investigated further.

Marvel and Rassweiler[105] obtained the substances as blue-green or greenish powders. The polymers were soluble (although with difficulty) in dimethylformamide, which enabled them to be separated from the phthalocyanine formed as a byproduct under these conditions. The polychelates could be reprecipitated from the dimethylformamide with chloroform, but these workers were unsuccessful in estimating the molecular weight of the compounds. The chelate polymers are similar to phthalocyanine in thermal properties, but in air they slowly decompose at 350° and above.

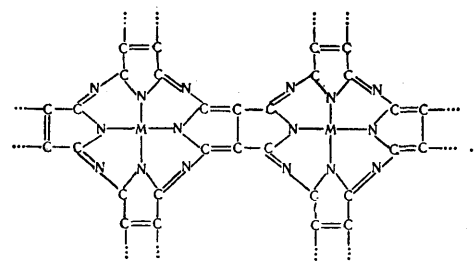
Somewhat later Marvel and Martin[106] described the preparation of a polymeric phthalocyanine of structure (IX) by a different method, based on the use of phthalonitrile and 3,3′,4,4′-tetracyanobiphenyls with copper bronze. These substances in various proportions were fused together at 275° for 3 h. The products were purified by extraction with acetone followed by agitation with sulphuric acid for 20 h. The insoluble residue dissolved in sulphuric acid on heating, but was not reprecipitated on cooling again. All these substances were dark blue with ametallic lustre. The infrared spectra, viscosity measurements, and analytical data show that the products have an extremely low degree of polymerisation. Such phthalocyanines decompose at 350° within 24 h.

Drinkard and Bailar's paper[107] also describes a polymeric copper phthalocyanine, obtained by the interaction of pyromellitoyl anhydride, cuprous chloride, and urea in the presence of a catalyst (ammonium molybdate) at 160° for 30 min. It is assumed that both linear (ribbon) and network structures are formed. Determinations of molecular and equivalent weights on the basis of elementary analysis and potentiometric titration give a mean molecular weight of about 4000, approximately corresponding to octameric phthalocyanine.

Epstein and Wildi[66] investigated the electrical properties of the polymeric copper phthalocyanine obtained by heating pyromellitonitrile with cuprous chloride and urea. They determined the Hall effect of the polychelate, and found that the compound has p-type conduction. The polymer is characterised by two states, one having an activation energy of 0.26 eV and a carrier density of 10^{16} cm^{-3}, while the second state, also characterised by p-type conduction, has a corresponding value after heat-treatment of 10^{18} cm^{-3}.

Joiner and Kenney[108] synthesised six-coordinate germanium phthalocyanine, in which two coordination positions were occupied by chloride anions. Hydrolysis led to the exchange of the anions for hydroxyls. This substance became appreciably darker on being heated. Examination of the infrared spectra showed that –O– bridging groups were formed with the production of polymeric germanium oxyphthalocyanine, for which the formula $(C_{32}H_{16}N_8GeO)_x$ was given.

Berlin *et al.*[109] synthesised very interesting and distinctive chelate polymers, which obviously contained only carbon, nitrogen, and metal atoms, while being close to the phthalocyanines in structure. The polymer was assumed to have a parquet structure:



Such polymers were obtained by reaction of the metals or their compounds with ethylenetetracarbonitrile in a vacuum at 160°–300°. An especially interesting phenomenon is the formation of films of polychelates having the above structure on the surface of metal strips when the latter are heated in ethylenetetracarbonitrile vapour under reduced pressure at 150°–400° for 5–20 h.[110]

The polymers are insoluble, infusible black materials, stable to the action of alkalis and dilute acids. It is interesting that the infrared spectrum exhibits no intense absorption bands in the range 700–3000 cm^{-1} apart from that at 2224 cm^{-1}, corresponding to the CN group.

The polychelates possess very intense broad electron paramagnetic resonance lines. Examination of the electrical properties of such polymers[111] shows them to have p-type conduction, while the dependence of the logarithm of the conductivity on the reciprocal of the temperature is similar to that for semiconductors possessing impurity conduction. Interaction of an equimolecular mixture of a metal acetylacetonate, ethylenetetracarbonitrile, and phthalonitrile yields copolymers which presumably have a ribbon structure[109].

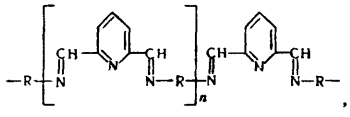
A further group of polybisdiazachelates, similar in structure to haemin and chlorophyll, have been described in a series of papers by Lautsch and his coworkers[112–114], who obtained various polymers and copolymers containing in the side-chains groups allied to the above compounds. Such chelate ligands were introduced into the polymer molecule either purely synthetically, by copolymerisa-

tion, or by incorporating prosthetic groups during polycondensation. As a result, polymers were obtained in which the main chain consisted of a linear or cross-linked ethyleneimine group and a polystyrene skeleton. Polycondensates of the type of polypeptides were finally obtained. In all cases the quantity of prosthetic groups was 0.01–1.0% of the main polymerised component. Several chelate polymers of these compounds with iron(II) were also obtained. Polychelates of this structure with a mesohaemin prosthetic group acted as oxidative catalysts.

Minne and Rochow[115] described the formation of polybisdiazachelates of copper with organosilylamines. Dimethylchlorosilane reacts with ethylenediamine to form a linear polymer of silylamine, treatment of which with anhydrous copper(II) chloride leads to rearrangement of the polymer chain with the formation of a silazane and simultaneous separation of ethylenediaminecopper chloride. Further treatment of the silazane with excess of $CuCl_2$ produces a cross-linked chelate polymer.

Similarly, beryllium chloride gives chelate polymers with the same silazane[116], one-third of the nitrogen atoms present in the original polymer taking part in the formation of chelate loops.

A synthesis of chelate polymers of distinctive structure has been effected also by Lions and Martin[117], who obtained polymeric Schiff bases from pyridine-2,6-dialdehyde with ethylenediamine, hexamethylenediamine, and benzidine. These were hard and infusible, their monomeric unit containing a terdentate group of nitrogen atoms

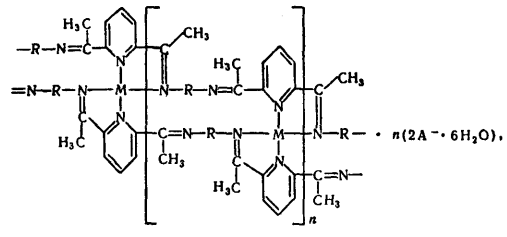


where R = $[CH_2]_2$, $[CH_2]_6$, p-C_6H_4.C_6H_4-p'. The first two polymers formed polychelates with bivalent salts of iron and cobalt, and the third with copper(II) salts. The chelate polymers, in contrast to the original Schiff bases, dissolved quite well in water, and were separated with difficulty from solution as the perchlorates or iodides Partial hydrolysis of the compounds might take place in solution, with separation of the metal hydroxides.

The structure of the substances remained obscure. Although these workers were inclined to the view that they had obtained polybistriazachelates, they pointed out[117] the possibility of such polymers existing as tetracoordinated compounds, *i.e.* as polybisdiazachelates. In this case one of the three nitrogen atoms in the terdentate group is not involved in the formation of coordinate links. Such a view seems to us the more correct, since the magnetochemical results obtained by these workers cannot give an unambiguous answer in the above cases, while the formation of a sexidendate chelate polymer is made extremely improbable also as a result of steric hindrance.

Depending on the conditions, polychelates varying in composition can be isolated, with a metal ion in all or in only a proportion of the chelate groups. A noteworthy polymer, isolated as the sulphate, is that of iron with the polymeric Schiff base from pyridine-2,6-dialdehyde and ethylenediamine, in which iron ions occupy all the coordination sites of the original macromolecule. It possessed appreciable ferromagnetism, its high molar magnetic susceptibility (0.15) being explained[117] by intermetallic interaction. However, it seems to us that the ferromagnetism of the polychelate is more likely to be due to contamination with the ferromagnetic oxide Fe_3O_4 than to interatomic interaction of the electron spins of the iron atoms. The likelihood of such a conclusion is supported also by the precipitation, observed by the American workers, of metal hydroxides from solutions of such polychelates and from solutions of non-polymeric complexes of analogous structure.

Compounds related to the above substances have been prepared by Terent'ev *et al.*[118] Starting from 2,6-diacetylpyridine, they synthesised a series of polyketimine derivatives of nickel, iron, and cobalt of the following structure:



where R = $[CH_2]_2$, $[CH_2]_6$, o-C_6H_4; M = Ni^{2+}, Fe^{2+}, Co^{2+}; $2A^-$ = Cl_2, SO_4. The resulting polybisdiazachelates were coloured powders, in most cases soluble in water or methanol.

Determination of the instability constants of several of the synthetic materials confirmed the structural formulae suggested for them, which were supported also by the magnetochemical results and the spectral characteristics of the polymers. Solutions of such compounds have anomalous viscosity, attributed primarily to dissociation of the macromolecular aggregates. Examination of the electrical properties of the polybisdiazachelates[75] showed that several of them possess a conductance which is typical of organic semiconductors.

6. Ion-Exchange Resins

A large and interesting group of polychelates are located on the borderline between two branches of chemistry — organic polymer and analytical chemistry. They are the macromolecular ion-exchange compounds. In some cases ion-exchange resins — more precisely cation-exchange resins — are able to segregate certain metal ions by forming coordinate bonds with ions of heavy metals. Here we shall give only a brief account of the main characteristics and methods of synthesis of cation-exchange resins, since several monographs and reviews have been published on this topic[119–126].

Among all the cation-exchange resins, we are interested only in those which form chelate loops. We shall not consider here cases in which the metal forms an insoluble salt of a macromolecular acid. We have already encountered representatives of this group of polymers. Without claiming to give a complete survey of chelate ion-exchange resins, we shall merely cite below a series of characteristic examples of polychelates having this structure.

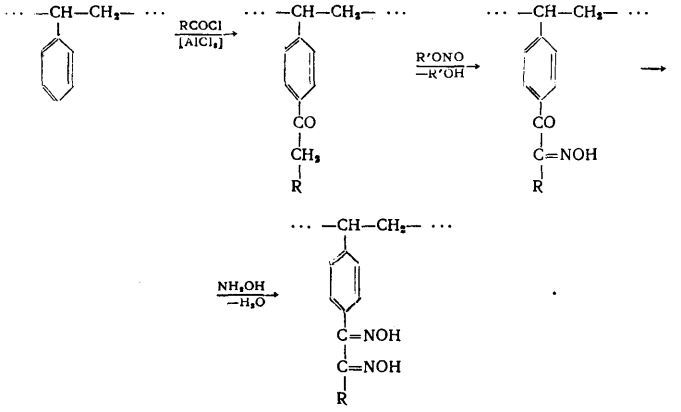
In the process of ion exchange, chelate compounds are usually formed only with feebly acidic cation-exchange resins. Nevertheless, these compounds possess enhanced

selectivity towards certain ions. For example, Smirnov and Blushvein[127] obtained a cation exchanger by the polycondensation of pyrogallol and formaldehyde, the selectivity of this compound for nickel and lead exceeding that for iron and calcium by a factor of 200. Selective cation-exchange resins of similar structure have also been prepared[128] from resorcinol, formaldehyde, and arsenic pentoxide with additions of cross-linking agents.

Despic and Kasanović[129] have describe the synthesis and polymerisation of an unsaturated β-diketone, methacryloylacetone (5-methylhex-5-ene-2,4-dione). In the presence of small quantities of ethylene glycol dimethacrylate as cross-linking agent, and after treatment with aqueous alkali, such a polymer forms polychelates with the uranyl and ferric ions. The resin loses its coordinated ions under the influence of acidic reagents. Similar behaviour is shown by resins obtained by the copolymerisation of methacroylacetone with methacrylic acid in the proportions 1 : 1 and 1 : 2 with additions of 10% of ethylene glycol dimethacrylate.

Cation exchangers based on cross-linked polystyrene or its copolymers are most widespread at the present time. For example, the Annual Report of the Chemical Research Laboratory at Teddington for 1954 [130] quotes data on the synthesis of polystyrene cross-linked with various substances containing chelate ligands. Such resins are capable of ion exchange. In particular, an investigation has been made of the possibility of complex formation by resins, containing amino-, carboxy-, amino-carboxy-, and sulpho-groups, with salts of bivalent copper, nickel cobalt, manganese, magnesium, calcium, and barium, tervalent lanthanum, and the alkali metals. Copper and nickel ions were shown to form the most stable chelates.

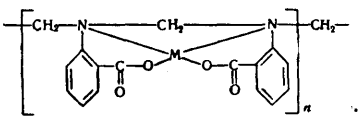
Štamberg *et al.*[131] obtained an ion exchanger based on cross-linked polystyrene, selective with respect to nickel, by the following scheme:



The structure of this cation exchanger is very similar to that of dimethylglyoxime, Chugaev's famous reagent for nickel ions.

Of course, it is not only cross-linked polymers and copolymers of styrene that are applicable as ion-exchange resins. Thus in 1957 a Czechoslovak patent[132] described the preparation by treatment of cross-linked chloromethylated copolymers of hydrocarbons with excess of amino-carboxylic acids, of a selective cation exchanger for the extraction of complexing ions. Another patent[133] claims the production of an ion-exchange resin which forms complexes selectively with copper and with palladium. Such a cation exchanger is obtained by condensing dihydroxybenzaldehyde with formaldehyde and then converting the polyaldehyde into a polyaldoxime.

An interesting complexing ion exchanger has been obtained by the polycondensation of anthranilic acid with formaldehyde[134,135]. The resulting polymer obviously contains chelate loops having the structure:



By the interaction of anthranilic acid, certain aromatic diamines, and formaldehyde, Gregor *et al.*[136] succeeded in obtaining a series of cation-exchange resins which gave stable polychelates with Cu^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, and Co^{2+}.

Bayer[137,138] investigated the relative stability of the complexes formed by copper, nickel, cobalt, zinc, cadmium, manganese, and uranium with the bis-*o*-hydroxyanil of glyoxal, and found that the metals can displace one another, at least partly, in the following sequence:

$$Cu > UO_2 > Ni > Co > Mn > Zn > Cd;$$

the further to the left is a metal in this series, the stronger the acid required to isolate it from its complex.

Bayer continued his investigation by studying polyaminophenols[139,140]. He condensed di- and tri-aminophenols with glyoxal, and obtained Schiff bases of high molecular weight. An especially interesting product was obtained by the polycondensation of 2,4,6-triaminophenol with glyoxal, yielding an insoluble black powder. Excess of glyoxal gives granular products, which is particularly valuable in view of Bayer's results. As in the case of glyoxal bis-*o*-hydroxyanil, the polymeric Schiff bases form macromolecular chelate compounds, which are able to yield back the metal on treatment with acids. Such Schiff bases are not hydrolysed by mineral acids of pH > 0.5. Nevertheless, such a resin proved to be extremely selective. Over the pH range 0–7 it does not bind alkali or alkaline earth metals at all. Bayer established that the polymer retains best of all the ions Cu^{2+}, UO_2^{2+}, and Ni^{2+}, even in the presence of a large excess of ions of other heavy metals.

Bayer also presented a paper on the preparation of these and similar macromolecular complexing agents[141] at the International Symposium on Macromolecular Chemistry, Wiesbaden (Germany), October 1959, where he described in particular the preparation of polyhydroxamic acids from a polymethacrylate. Such polymers formed stable polychelates with copper, iron, and uranium. Nevertheless, the selectivity of such ion-exchange resins was considerably lower than that of the resins described above. It is true that they possess higher mechanical and chemical stability than the polymeric Schiff bases, but their capacity for metals is rather lower.

It is interesting that chelate polymers can themselves extract ions from solutions, and then act as anion exchangers. Such an exchanger has been obtained[142] by the interaction of copper(II) and cobalt(II) salts with cross-linked polyethyleneimine. The chelate polycation was so stable that its combined copper could not be replaced by zinc, nickel, or cobalt. Only in strongly acid medium did this polymer lose its metal ions.

Nonogaki has subsequently obtained another anion-exchange resin of the same type[143]. A copolymer of polyethyleneimine and dichloroethane gave a stable complex with copper salts. Such a polychelate can be used as a strongly basic anion-exchange resin. Similar results were obtained in the synthesis of chelate polymers of cobalt with copolymers of *o*-bis-2-aminoethylaminomethylbenzene and dichloroethane.

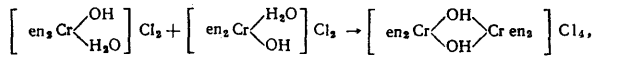
7. Hydroxo-Bridged and Related Compounds

The work discussed above does not exhaust the chemistry of chelate polymers. The small but distinctive group of hydroxo-bridged compounds and their structural analogues should, in our opinion, be included among polychelates. These chelate polymers lie on the borderline between the chemistry of inorganic polymers and the chemistry of polychelates. Here, too, we shall deal only with a few of the most important examples of compounds of this type.

These compounds are complexes in which metal atoms are linked together by hydroxo-bridging groups. Their formation may be accompanied by substitution by anions, or by conversion of hydroxo- into oxo-bridging groups. These processes may take place simultaneously.

Hydroxo-bridged and related compounds provide an example of those rare cases in which a chelate polymer is formed with molecules containing less than two pairs of donor groups.

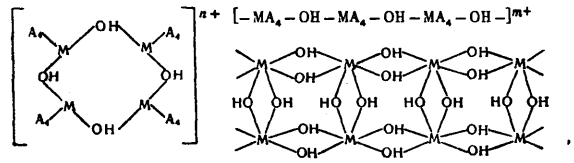
The first chemists to isolate hydroxo-bridged compounds were probably Gentele[144] and Jörgensen[145]. During the early 1890's these compounds were investigated by Pfeiffer[146,147], who suggested that the two metal atoms in them could be linked by hydroxo-groups. On the basis of modern ideas, the reaction which he described can be written as follows:



where en represents an ethylenediamine molecule.

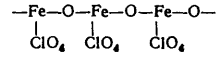
Subsequently, the amount of work done on hydroxo-bridged and related compounds increased markedly. Thus by 1930 Gmelins Handbuch, for example, listed[148] many tens of such compounds of cobalt, but consideration was confined to bridged complexes containing not more than four central atoms. Mellor[149] also cited a large number of papers describing hydroxo-bridged and related compounds, devoting more than fifteen pages, for example, to cobalt compounds having this structure.

In fact, the process of hydroxo-bridge formation may not be completed at a definite stage. Pfeiffer[150] suggested that the first stage in such a process is hydrolysis of the salts. A little later Kullgren[151] showed that the degree of hydrolysis increases with rise in temperature. It is affected also by the pH of the solution and the nature of the anion[152]. If insufficient alkali for complete neutralisation is added to such a solution, polymerisation occurs instead of precipitation of a hydroxide or a hydroxo-salt. For example, Bjerrum showed in a series of papers[153-155] that the resulting structures are of similar size to colloidal particles. Riess and Barth[156] found that Bjerrum's solutions contained substances of ionic weight 400–1000, and postulated the existence of polyhydroxo-compounds of three types, with cyclic, linear, and network structures. Thus the following structural formulae can be written in the case of six-coordinate tervalent metals (M), which most often form such compounds:

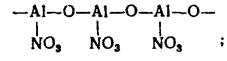


where A is a coordinated molecule or ion.

Hydroxo-bridging groups can be converted into oxo-groups under the influence of heat. Such a process can occur also on the slow addition of alkali to solutions of hydroxy-compounds. Jander and Jahr[157] found that addition of alkali to ferric perchlorate solutions produces dimeric compounds, first hydroxo and then oxo. A large quantity of alkali leads to the formation of such substances as:



These workers found that the addition of two moles of ammonia to one mole of aluminium nitrate results in the formation of the structure:



addition of alkali does not precipitate the hydroxide, but the degree of polymerisation is increased. Zirconium perchlorate behaves similarly.

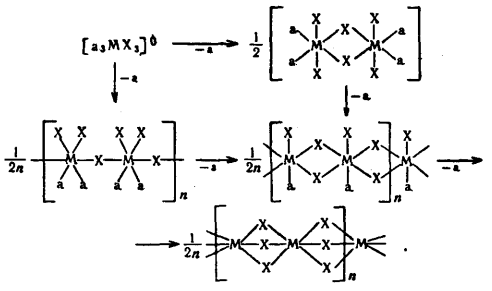
More recently Bradley[158] has discussed, on the basis of some earlier work[159], the three-dimensional structure of metal alkoxides. All such compounds of general formula $M(OR)_n$ (where n is the valency of the metal) form polymers corresponding to the coordination number of the metal. In several cases Bradley indicates the minimum degree of polymerisation (x) of such alkoxides $[M(OR)_n]_x$: depending on the valency of the metal, x varies from 2 to 8. He also states that, with the same radicals R and in the same group of the Periodic System, the degree of polymerisation x increases with increase in size of the metal atom.

Thus most of the known hydroxo- and oxo-bridged compounds are macromolecular. From the point of view of coordination theory, hydrous metal oxides can be included in this class of substances. For example, Graham and Thomas[160] assume the compounds to be complexes of zero charge. On this basis it is easy to explain such properties of hydrous oxides as the diminution in their reactivity produced by the aging of solutions with time or on heating, and also their ability to retain certain anionic impurities even after prolonged washing. It must be noted, however, that this theory has been subjected to serious criticism based on X-ray investigations[161].

In this section we have repeatedly used the term "hydroxo-bridged and related compounds". Among these "related compounds" must be included complexes in which metal atoms are linked by bridging atoms of oxygen, sulphur, nitrogen, or halogens, or by some of their simplest

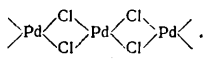
derivatives. We have just described above a series of oxo--compounds belonging to this group of polymers. Jensen's mercaptides[91], which have been discussed earlier (p. 675), should probably be included in this group of substances. Let us consider some other work on compounds related in structure to hydroxo-bridged polymers.

Substances of this type can be formed in some cases, for example, in the synthesis of amido-complexes. In general a complex $[a_3MX_3]^0$ can undergo the series of reactions:



A comprehensive investigation of the conditions for such a reaction has been undertaken by Schmitz-Dumont[162], with $[Co(NH_3)_6](NO_3)_3$ and several other substances as examples. He obtained a series of amido, hydroxo-amido, and amido--alkoxo complexes of tervalent cobalt and chromium having the above structure (X = NH_2, OH, O, OR, or combinations thereof; M = Co^{3+}, Cr^{3+}). The products were amorphous powders, similar in properties to other macromolecular coordination compounds.

The interesting paper by Shaw[5] states that X-ray studies of complex compounds have shown that the simple formula AB_n cannot be used to determine the coordination number of the central atom A, which often exceeds n. For example, ferric chloride in the solid state is a polymer of coordination number 4. Palladium chloride molecules have a similar structure, forming a planar polymer in which chlorine atoms form bridges



Caesium copper(II) chloride $CsCuCl_3$ contains the ion $[CuCl_3]_n^{n-}$ of indefinite chain length. Shaw considers that a similar structure is possessed by HgI_2, MoS_2, WS_2, and several other compounds.

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Several chelate polymers containing various chelate loops have been discussed. Research has been concerned mainly with the thermal properties of polychelates, and most of the experimental work on the chemistry of chelate polymers has been on these lines. Unfortunately, little published information can be found on the electrical properties of chelates; reports on the structure of the chelate loops in the polymers, the overall structure of the macromolecules, or their spatial arrangement are few.

Nevertheless, a few conclusions on the properties of chelate polymers can be reached from an examination of the literature. The thermal stability of polychelates greatly depends on whether the metal ion is located in the main polymer chain, when relatively thermostable materials are formed, or in side-chains, in which case no appreciable increase in thermal stability is observed. The properties of polychelates are greatly affected by the structure of the chelate loop. For example, among polybisdioxachelates the beryllium polymers are the most interesting, while among the bisdiaza-compounds it is the iron and copper derivatives. In several cases films and filaments can be obtained from chelate polymers, but they are sometimes quite unsuitable for industrial processing.

Chelate polymers having interesting electrical properties, those of semiconductors, catalysts, etc., are attracting attention. These specific characteristics are usually inherent in polychelates containing a system of conjugated bonds, and also in compounds which are in some way ordered as a planar or three-dimensional network. But work on these lines is at present only sporadic.

The chemistry of chelate polymers forms a new branch of polymer chemistry. The immediate difficulty is to visualise the mechanism by which polychelates are formed. The physicochemical properties of such compounds are not always clear; difficulties will undoubtedly be encountered in the industrial utilisation of polymers. Nevertheless, the structural characteristics of polychelates will make it possible in the future to synthesis compounds having the most varied combinations of properties.

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