Coordination Chemistry Reviews, 16 (1975) 195—225

PROBLEMS OF COMPLEX FORMATION WITH MACROMOLECULAR LIGANDS

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(Received June 12th, 1974)

CONTENTS

A. INTRODUCTION

In this review paper an attempt is made to consider problems of formation, structural characterisation and ways of utilization of a new class of high-molecular weight compounds. These comprise coordination compounds of transition, alkali and alkali-earth metal ions, with macromolecular ligands.

The problem of complex formation with macromolecular ligands overlaps areas of various allied sciences with the prospect of production, investigation and utilization of compounds exhibiting unusual behavior (due to their macromolecular character). It is this unusual character which generates interest in the class of compounds under consideration. Coordination chemistry provides examples of complexes incorporating in the same molecule a variety of structural types of coordination centers possessing defect, unusual or mixed composition. Bio-inorganic chemistry supplies macromolecular complex models which can participate in such reactions as redox, transesterification or transamination, reversible interactions etc. In macromolecular chemistry we find many examples where the reactivity of the complexing groups is determined by the covalent bonding of "separate" ligands in a macromolecular unit.

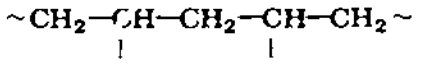
B. PROPERTIES AND STRUCTURAL CHARACTERISTICS OF MACROMOLECULAR LIGANDS

Although macromolecular ligands may be as numerous as low-molecular weight complexing compounds, so far few types of synthetic polymer ligands have been exhaustively studied. These are: polyacrylic and polymethacrylic acids, polyketoesters and polydiketones, polyaminoacetic acids, linear or ma-

crocyclic polyesters, polyvinylpyridines and other nitrogen-containing polyligands and sulphur- and phosphorus-containing complexing polymers. Of the naturally occurring polyligands, polysaccharides of the cellulose type and nucleic acids have been most thoroughly investigated.

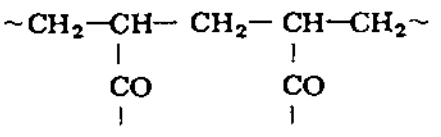
In spite of the very different synthetic routes leading to the macromolecular compounds, and of the differences in characteristics of the functional (complexing) groups on the chain, as well as in the structure and conformation of the main polymeric chain carrying these groups, these systems exhibit similar features characteristic of macromolecular ligands in general. These derive from the polyfunctional nature of macromolecular complexing compounds. The reverse is the case with low-molecular weight complexes with all of the ligand molecules possessing the same structure and consequently exhibiting the same properties provided the substance is properly purified.

For some time, it has been recognised that nonuniformity of individual complexing groups within ligating polymers is a characteristic of such polymers. Thus, Gregor [1] who was the first to prepare polyacetonylacetone via acetylation of polyvinylmethylketone, reports $-CO-CH_3$ groups along with diacetylated groups $-C(CH_2-CO-CH_3)_2$ or cyclic groups, (1),



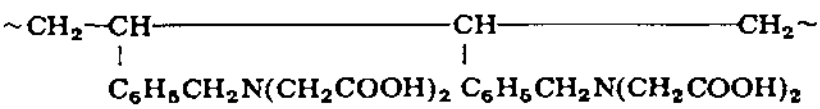
(1)

occurring in polyacetonylacetone chains, (2).



(2)

Davydova and co-workers [2] have carried out the ester condensation of dicarboxylic esters to produce poly-β-ketoesters, $\sim CH_2-CO-CH(COOR)-CH_2\sim$. These authors note the possibility that the polymeric chain comprises both ketonic and carboxylic groups. In building up polymeric iminodiacetic acid [3,4], (3),

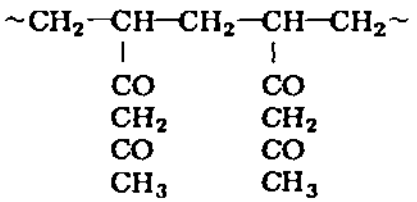


(3)

a variety of functional groups, for example, secondary and tertiary aminocarboxylic and aminomethylcarboxylic groups, $\geq NH$, $\geq N$, $-NHCH_2COOH$, $\geq NCH_2COOH$, were observed as by-products. These occur on the chain along with residual primary amino groups. Wolf and Hering [5] have succeeded in the fixation of only the iminodiacetic groups on the polymer by use of chloromethylated polysterene and iminodiacetic ester.

The efficiency of complex formation involving macromolecular ligands is

influenced not only by the character of the functional groups, but also by their distribution along the polyligand chain. It is known that in some cases polymeric ligands (e.g. polymethacryloylacetone, polyvinylacetonylketone or polyvinylacetoacetate) whilst participating in binding metal ions (e.g. of nickel) utilise far below the total number (up to 50%) of complexing groups [6]. These occur at every monomeric unit and cause steric hindrance, see



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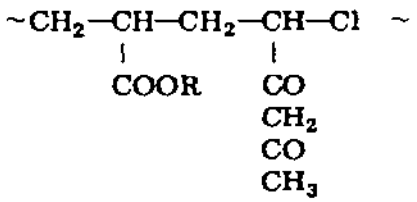
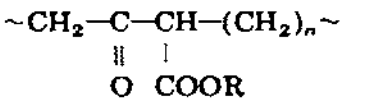


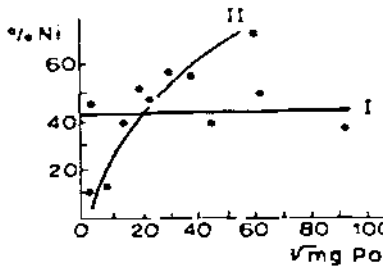
(5)

Fig. 1, I and (4,5). The efficiency of complex formation may be increased by using co-polymers in which functional groups do not occur at all of the monomeric units, Fig. 1, II. With polyketoesters, all the complexing groups bind ions such as copper. In such cases the functional groups are separated by several methylene units instead of being situated at every, or at every other carbon atom in the chain. Such is the case with polydiethylazelate, polydiethylsebacate, polydiethyldecanoate and polydiethyldodecanoate [7], (6).



(6)

$n = 5,6,8,10$



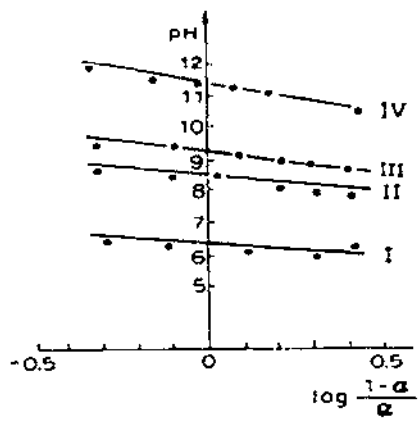
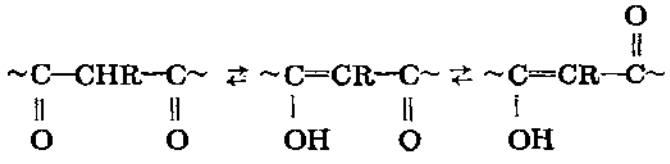


Fig. 1. The efficiency of complex formation with Ni^{+2} of polymethacryloylacetone, I, and copolymer of methacryloyacetone with butylmethacrylate, II. % Ni^{+2} in polymer vs. [Ni^{2+}] *mg*, in solution.

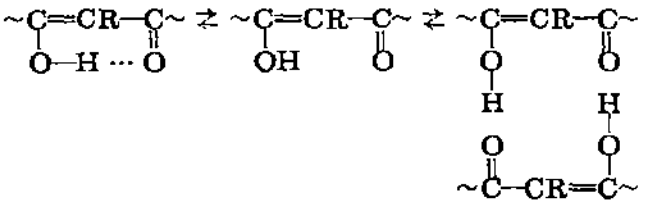
Fig. 2. The plot of apparent dissociation constant of polydiethylazelate I, polydiethyldecanoate II, polyvinylacetoacetate III and acetoacetate IV versus degree of ionization.

In preparing and using such polyligands containing functional groups which are subject to keto—enol, —CO—CH_2— ⇄ —C(OH)=CH—, ketoimine, —CO—NH— ⇄ —C(OH)=N—, or keto—imide, —C(—NH)—NH ⇄ —C(NH_2)=N— tautomerism, the characteristics of tautomeric transformations must be taken into account. Thus, enolization is sterically hindered in polymeric β-ketoesters and β-diketones [8] for this involves deformation of a macromolecule itself as well as of functional groups. This results in a percentage decrease in the extent of tautomerism on the one hand (Table 1) and in nonuniformity of the *cis*-enol fraction in the polymeric ketoenol (7). The weakening of intra-



keto-form *cis*-enol *trans*-enol (7)

unit hydrogen bonding in the case of the *cis*-enol form causes non-uniformity in the enol fraction of β-carbonyl type polymers. In the limiting case rupture of the hydrogen intramolecular bonds results, to give rise to *cis*-enol forms either without hydrogen bonding or participating in intermolecular (inter-unit) hydrogen bonding [9], (8).



(8)

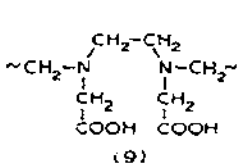
Enolizability and the acidity of keto—enol tautomeric compounds are known to be related [10]; the latter is determined by the structure of the β-dicarbonyl compound, whereas the keto—enol equilibrium depends upon the ratio of acid dissociation constants of the tautomers. Thus the last two of the above structures (that with the open OH-group and that with the OH-group involved in intermolecular hydrogen bonding) which occur in the enol fraction of polymeric β-ketoesters, Table 2, account for the higher acidity of this type of polymeric ligand as compared to their low-molecular weight analogues, for example, to acetoacetate or terephthalyl diacetoacetate, see Fig. 2. In turn, the acidity of macroligands influences the efficiency of complex formation. The ability of macroligands to form complexes depends to a certain degree on the nature of the main chain: whether it is a polymeric alkane or polyaromatic compound produced via polymerization of corresponding monomers, or otherwise contains heteroatoms, representing polycondensation polymers. Polymeric iminoacetic acids with functional groups occurring on different polymeric matrices may serve as examples (9), polyethyleneimino-

TABLE 1

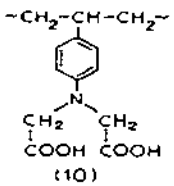
Enolizability of macromolecular and low-molecular β-ketoesters in solvents of various polarity[a,b]

	Solvent								
	CH_3COOH	CH_3OH	$(CH_3)_2CO$	$CHCl_3$	C_2H_5OH	$CH_3COOC_2H_5$	C_6H_6	$(C_2H_5)_2O$	CCl_4
1 Polydiethylacetate									
E(%)	–	2.7	–	2.3	2.5	–	3.3	3.7	3.2
K	–	0.03	–	0.02	0.02	–	0.03	0.04	0.03
2 Polydiethyldecanoate									
E(%)	5.0–5.6	–	6.0	–	–	4.6	4.6	4.6	4.5
K	0.05	–	0.06	–	–	0.05	0.05	0.05	0.05
3 Ethyl ester of valerylvaleric acid									
E(%)	–	1.1	–	–	1.8	–	2.7	3.7	–
K	–	0.01	–	–	0.02	–	0.03	0.04	–
4 Polyvinylacetoacetate									
E(%)	6.2–7.0	–	6.9	6.9	–	6.9–7.6	–	–	–
K	0.07	–	0.07	0.07	–	0.07–0.08	–	–	–
5 Acetoacetate									
E(%)	6.75	6.9	7.4	8.2	11.5	13.1	18.2	30.0	35.0
K	0.06	0.07	0.08	0.089	0.13	0.15	0.22	0.43	0.64
6 Polyterephthalyldiacetate									
E(%)	–	–	–	–	–	12.7	–	18.5	–
K	–	–	–	–	–	0.15	–	0.23	–
7 Terephthalyldiacetate									
E(%)	17.9	–	–	–	–	24.3	–	41.8	–
K	0.218	–	–	–	–	0.32	–	0.72	–
8 Polyterephthalyldiacetoacetate									
E(%)	–	4.3	15.6	–	–	22.9	–	–	–
K	–	0.045	0.184	–	–	0.30	–	–	–
9 Terephthalyldiacetoacetate									
E(%)	38.4	–	–	46.1	–	49.9	63.8	–	83.2
K	0.62	–	–	0.85	–	0.99	1.76	–	4.95

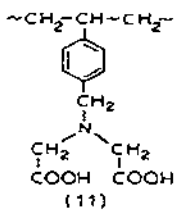
[a] *E*(%) is the degree of enolization defined by Dieckman's bromometric method. [b] $K = E/(100 \cdot E)$.



(9)



(10)



(11)

acetic acid [11]; (10), polystyreneiminodiacetic acid [12]; (11) polymeric iminodiacetic acid [13].

The complexing power of macromolecular ligands also depends upon the arrangement of functional groups relative to the main chain. The shorter the distance between them, the lower the efficiency of complex formation because of steric hindrance. As illustrated by complexes of the vinylpyridine series, the complexing power of the ion exchangers (ionites) below varies substantially even though the nature, basicity and concentration of these are

Macromolecular ligand	pK_a	log $K_{stability}$ Cu^{2+}
Poly-4-vinylpyridine	5.35	4.44
Poly-2-vinylpyridine	4.42	1.30
Poly-5-vinylpyridine	5.25	3.10

very similar [17]. Studies on the complex formation with low-molecular weight analogues, vinylpyridines, demonstrate no such variation [18].

The complexing characteristics of insoluble macromolecules are also strongly influenced by the extent of cross-linking in the ligand. Thus, Saldadze and co-workers [19] report the colouration of copper complexes with polyvinylpyridines to change from blue to deep green when increasing the extent of cross-linking (as measured by the percentage of divinylbenzene) from 4 to 16. To judge from the colour evidence, a conversion of planar coordination centers into tetrahedral ones occurs. This change in stereochemistry results

TABLE 2

Acidity of β-ketoesters and their tautomeric forms in dioxane—water medium (4 : 1 volume ratio); 25 ± 0.5°; 0.1 *N* $NaNO_3$

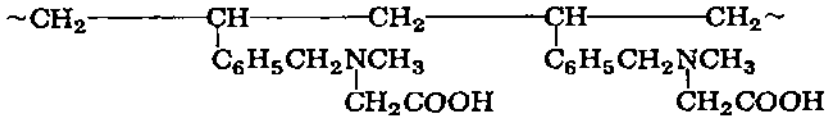
	Ligand	K_T[a]	pK_a	pK_{enol}
1	Acetoacetate	0.086	11.4	10.3
2	Polyvinylacetoacetate	0.70	10.6	9.2
3	Polydiethyldecanoate	0.50	9.7	8.4
4	Polydiethylazelate	0.026	8.0	6.4
5	Terephthalyldiacetoacetate	0.60	10.6	10.2
6	Terephthalyldiacetate	0.18	7.9	7.1
7	Polyterephthalyldiacetoacetate	0.20	7.8	7.0
8	Polyterephthalyldiacetate	0.06	11.2	10.0

[a] K_T = keto—enol equilibrium constant; K_a = acid disocciation constant; K_{enol} = acid disocciation constant of enol.; pK_a and pK_{enol} values quoted for brevity.

from an increase in steric hindrance to complex formation with a macromolecule, which is also known with low-molecular weight coordination compounds.

Complexing groups in a macromolecular ligand may exist in conformations different from that required by the preferred stereochemistry of a given metal ion. Functional groups are frequently statistically distributed over a macromolecule so that both the more favourable conformations and the less favourable will occur. Hence, the formation of a given spatial structure required by the electronic configuration of an ion, M^{n+}, is followed by a conformational change in the ligand so that it may assume an appropriate orientation. The change is associated with a greater energy loss, the more the chain conformation differs from ideal and the less flexible is the macromolecule. Since the coordination bond energy remains constant for a given metal—ligand pair, the stability of polymeric complexes is proportional to the flexibility of a macromolecule and to the set of conformations it can generate.

This is particularly true of insoluble cross-linked ligands, e.g. ion exchangers, which exhibit rather small chain flexibility and offer quite a limited set of chain conformations. According to a scheme by Hering [20] (Fig. 3) suggested to account for the efficiency of complex formation with sarcosine resin, (12),



(12)

the two adjacent polystyrene chains deform and separate from each other to give rise to metal complexes of corresponding stability. The extent of deformation (D values) ranges from zero (an ideal conformation) to values exceeding that of the complexing energy, B (conformations hindering further participation of ions in the reaction). These limitations result in a decreasing coordinative saturation of the central metal ion and may give rise to stereochemical distortion of the coordination centers and also to a lowering of macromolecular complex stability.

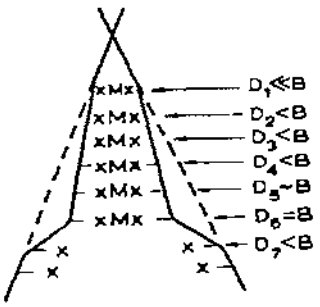
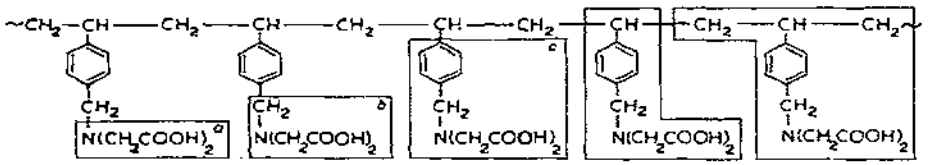


Fig. 3. The scheme of complex formation of monofunctional sarcosine resin with transition metal ions following Hering [20]. D is chain deformation and B is energy of complex formation.

The above examples show the important effects caused by the absence, or presence, of side groups as well as by the spatial arrangement of complexing groups over the macromolecular ligand chain, upon the efficiency of complex formation with macromolecular ligands, both soluble and insoluble (the latter of reticular polyligand type or of ion exchanger type).

To examine the characteristic properties of macromolecular complexing compounds it is worth-while comparing these to low-molecular weight analogues. Proper choice of such an analogue is of importance. The latter must contain a given functional group bound to the nearest unit of a macromolecule in such a way as to provide the closest correspondence between both electronic and steric factors operating in the polymer and in the model compound. Relatively few compounds offer no difficulties in deciding upon an appropriate low-molecular weight analogue. A number of possible models exist, for instance, with polyiminodiacetic acid [20] (13). Comparison of the



(13)

acid dissociation constants of the ligands, pK_1 and pK_2, as well as of the stability constants of the complexes shows how essential it is to define an appropriate fragment of the chain as a model. Therefore in comparing the

Fragment of a polyligand	pK_1	pK_2	$pK_{Cu^{2+}}$	$pK_{Ni^{2+}}$
a iminodiacetic acid	2.54	9.12	10.55	8.26
b *N*-methyliminodiacetic acid	2.46	9.73	11.09	8.73
c *N*-benzyliminodiacetic acid	2.36	9.02	10.29	7.97

complexing characteristics of macromolecules an indication of which low-molecular weight ligands serve as model compounds should be made clear.

C. STRUCTURAL CHARACTERISTICS OF COMPLEXES WITH MACROMOLECULAR LIGANDS

The occurrence of unoccupied or partly occupied orbitals in the metal atom and the tendency of the metal atom to overcome its electron deficiency at the expense of the electron pairs which belong to the functional groups of the ligand is known to be a controlling factor in the formation of ligand-to-metal bonds. In this respect the processes of complex formation with both high- and low-molecular weight compounds are alike. The principal point of difference is the following. With low-molecular weight ligands, most metals utilise sp^3d^2 or d^2sp^3 hybridization to give an octahedral arrangement of ligands in a six-coordinated complex, or d^2sp or sp^3 hybridization to give four-coordinated

planar or tetrahedral structures, respectively. With high-molecular weight ligands, orbital vacancies on the metal may remain due to the specific properties inherent in a macromolecule. With low-molecular weight compounds residual vacancies participate in bonding with solvent, another ligand etc. Hence complex stability is lower as a rule in the case of macromolecular ligands compared with low-molecular weight analogues, and with insoluble polymers it is even lower than with soluble species [21]:

Ligand	Monomeric 4-CH_3-pyridine	Soluble poly-4-vinylpiridine	Insoluble co-polymer of 4-vinylpyridine and divinylbenzene
$\log K_{\text{stability}}\ Cu^{2+}$ (potentiometric)	2.56	2.40	2.20

On the contrary, Teyssie [22] reports values of the formation constant, $K = [ML_2]/[M][L]^2$, and of the substitution constant, $B = [ML_2][H]^2/[LH][M]$, to show but small variation in going from complexes of a number of divalent ions with polymeric methacrylylacetone to those with a low-molecular weight analogue, pivaloylacetone:

M^{2+}	$\log K_{\text{pol.}}$	$\log B_{\text{pol.}}$	$\log K_{\text{mon.}}$	$\log B_{\text{mon.}}$
Cu	22.8	—6.0	22.0	—5.0
Ni	17.4	—11.4	16.2	—10.8
Co	17.1	—11.7	15.8	—11.2
Mn	15.1	—13.7	13.4	—13.6

Nevertheless, the stability of complexes with macromolecular ligands should be lower as a rule compared with low-molecular weight analogues, irrespective of the nature of functional groups. Table 3 shows the stability constants of a number of complexes, mainly of copper, with poly-β-ketoesters of various structures and of related model compounds [23].

Table 3 shows that poly-β-ketoesters are stronger acids than the model compounds by 2—3 orders of magnitude and yet give rise to complexes less stable by 3—5 orders of magnitude compared with low-molecular weight compounds of similar structure. The lower stability of the polymeric complexes and higher acidity of the polymeric complexing agents originate from the non-uniformity of the enol fraction with high-molecular weight compounds (see above). Note that the experimental values of stability, substitution or equilibrium exchange constants represent averages since these must vary along a macromolecular chain of the complex due to the non-uniformity of the enol fraction and the highly strained nature of *cis*-enol units involved in intermolecular hydrogen bonding [24].

In Fig. 4, the dependence of polymer acid, pK_a, is plotted against its com-

TABLE 3

Stability constants of complexes with β-ketoesters; dioxane—water (4 : 1 volume ratio); 25 ± 0.5; 0.1 *N* $NaNO_3$.

	Ligand	Cu^{2+}			Ni^{2+}	
		pK_a	$\log \beta_2^a$	$-\log B$	$\log \beta_2$	$-\log B$
1	Polydiethylazelate	6.4	8.0	4.8	7.5	5.2
2	Polydiethyldecanoate	8.4	10.7	6.1		
3	Polydiethyldodecanoate	9.8	12.5	7.1		
4	Polydiacetylglutarate	10.0	12.7	7.4		
5	Diethyl ester of acetylglutaric acid	11.4	15.2	7.6	13.2	9.6
6	Polyterephthalylacetoacetate	7.0	9.5	4.5	8.9	5.1
7	Terephthalylacetoacetate	10.2	14.5	6.8		
8	Polyvinylacetoacetate	9.2	14.4	4.0	10.5	7.9
9	Acetoacetate	11.4	17.2	5.6	14.8	8.0
10	Polyterephthalyldiacetate	7.1	10.1	3.8		
11	Terephthalyldiacetate	10.0	15.8	4.2		

[a] *B* is the substitution constant (see p. 203).

plexing power, log β as exemplified by copper derivatives of β-ketoesters, Table 3. One can distinguish two correlations. α- and α, γ-substituted derivatives of acetoacetate: polydiethyldecanoate, polydiethyldodecanoate, diethyl ester of acetylglutaric acid and its high-molecular weight analogues, polydiethylacetylglutarate and terephthalyldiacetoacetate, and its high-molecular weight derivative, polyterephthalyldiacetoacetate, all follow the first type of correlation (the lower line). The second type (the upper line) is represented by non-substituted acetoacetate and its γ-derivative, terephthalyldiacetoacetate, and their high-molecular weight analogues (polyvinylacetoacetate and polyterephthalyldiacetoacetates).

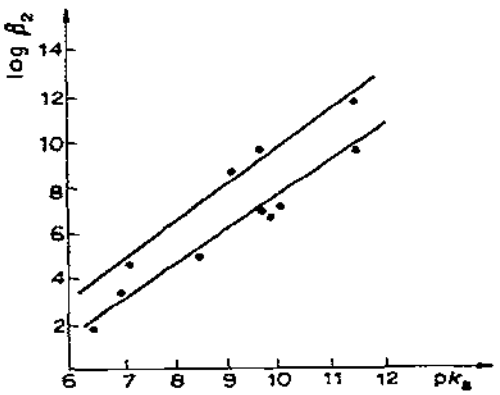
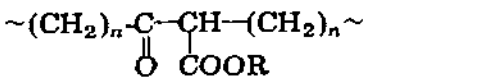


Fig. 4. A plot of 1/log K_a versus log β_2 for the polyligands presented in Table 3.

The existence of the above two correlations shows the structure of functional groups to be a controlling factor in determining the acidity and complexing characteristics of a macromolecular ligand. Within the same type, macromolecular complexing agents are structurally related to each other and to their low-molecular weight analogues and originate complexes of similar character. There is also a close correlation [25] between macromolecular complex stability and C—C stretching frequency of the chelate ring (similar to that observed with low-molecular weight complexes):

Ligand	$\nu(cm^{-1})$	$\log \beta_2$
Polymethacrylylacetone	1567	22.8
Polyterephthalyldiacetate	1575	15.2
Polyvinylacetoacetate	1595	14.4
Polydiethyldecanoate	1600	10.7
Polyvinylacetonylketone	1600	7.0
Polydiethylazelate	1605	8.0

Among the structural features of macromolecular ligand complexes the possibility of "isolation" of coordination centers with respect to each other should be considered. Thus, ESR studies [7] on copper complexes with poly-β-ketoesters exhibit diamagnetic dilution of the coordination centers by polymethylene fragments:



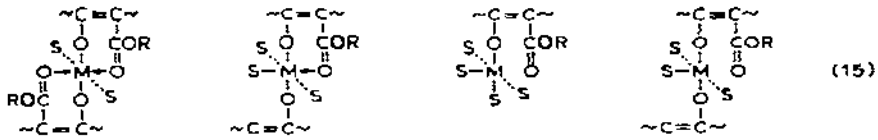
(14)

$n = 2,5,6,8,10$

Due to the dilution, each of the coordination centers in the polymer appears to be more isolated than those in copper complexes with acetoacetate or acetylacetone. This gives rise to HFS (hyperfine structure) with splitting of the order of 35 oe, observed only with polyligands of longer intracenter polymethylene fragments (n equal to or exceeding 6). The same feature is characteristic of low-molecular weight complex compounds only when in solution. As for magnetic susceptibility and magnetic moment values χ and μ_{eff} these parameters of polymer complex compounds (e.g. belonging to the same poly-β-ketoester or β-diketonic type) should also be thought of as averaged characteristics, since, according to the foregoing, coordination centers of various symmetry and hence of various magnetic properties may be formed within the same macromolecule.

Even if uniform in composition and in distribution of functional groups, a macromolecular ligand may be expected to combine with metal ions to give rise to a variety of types of coordination centers. Interaction with di- or trivalent ions may result in the formation of ionic or coordination binding, depending on the tendency inherent in the ions. The lower the stability con-

stant of the resulting complex, the higher the probability of ionic type bonding, and vice versa. Thus, Davydova, Plate and co-workers [24] suggest the formation of various types of coordination centers in transition metal complexes of poly-β-ketoesters and poly-β-diketones (15).



(15)

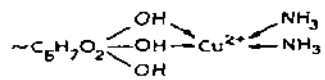
According to Hering [20] even a uniform polymeric iminodiacetic acid may act as a monobasic or dibasic acid to give rise to purely ionic or more covalent bonding in the same macromolecule.

In the formation of most stable coordination centers, quite a number of polyligands participate via two functional groups per divalent metal ion, ML_2. Hydrated ions may also give rise to centers of composition, $ML_2(H_2O)_n$. Solvents used in the complexing processes may enter the coordination sphere to produce centers of the type $ML_2(H_2O)_nS_m$. This is not necessary in the case of Cu^{2+} ions (d^9-configuration) which are most likely to give coordination centers of planar structure. With other transition metal ions Ni^{2+} (d^8), Co^{2+} (d^7), Co^{3+} (d^6), Mn^{2+} (d^5), Mn^{3+} (d^4), of which the octahedral or tetragonal environment is characteristic, the structure of the coordination center undergoes a distortion. In practice the coordination sphere of such ions when bound to a polycomplex may involve any anion that occurs in the reaction mixture.

Of course, examples of polymeric complexes with non-uniform composition or "defect" structure in the coordination centers are not only restricted to β-ketoesters and polyiminodiacetic acids. Binding of low-molecular weight ligands present in the reaction medium to saturate coordination centers will occur with natural macromolecular complex compounds.

Swensson and Tornell [26] report quite a number of coordination centers in Zn^{2+} complexes of cellulose xantogenates which originate from functional groups of various spatial orientation with respect to the main chain; these vary in thermodynamic stability and reactivity towards acids.

Cellulose itself also gives rise to mixed ligand complexes [27]. At present, the formation of copper complexes of cellulose with the coordination sphere containing various ligands is regarded as most probable [28] (16). Complex



(16)

formation occurs first at secondary C_2- and C_3-hydroxyls rather than at primary ones. It is also suggested that primary hydroxyls may contribute to the center formation via ionic type bonding. Jayme [29] reports similar structures to occur in mixed complexes of cellulose and other transition metals (Ni^{2+}, Zn^{2+}, Cd^{2+} etc.).

Cellulose and its analogues may give complexes via coordination or ionic

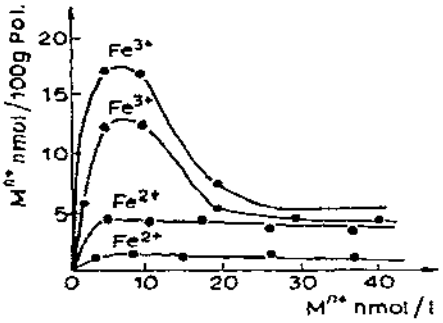


Fig. 5. The efficiency of complex formation of Fe^{+2} (lower curves) and Fe^{+3} (upper curves) (in mmol per 100 g of polymer) with cellulose, 45°, 60 min.

type bonding. Sorption of Fe^{2+} ions by cellulose takes place regardless of the temperature and the reaction time. Treating of sorbent with diluted acids results in a ready desorption, see Fig. 5. These ions react with the macromolecular ligand in an ionic way. On the contrary, with Fe^{3+} ions the amount of sorbate depends upon temperature, time and concentration of metal ions, suggesting the formation of a complex with cellulose macromolecules; in this case, desorption can be effected only by using 2 *N* or even 5 *N* rather than dilute hydrochloric acid [30,31].

Thus macromolecular complexes are characterised by a modified composition of the coordination center as compared to that in low-molecular weight models, by undersaturation of complexing ions and by the formation of coordination centers with mixed ligands.

This results, as a rule, in a lower stability of these complexes with macromolecular ligands as compared with those of low-molecular weight complex compounds of regular stoichiometry.

D. PROCESSES OF MACROMOLECULAR COMPLEX FORMATION

Up to the present, the characteristics of macroligands as substances of polymeric nature have not generally been understood in dealing with processes of complex formation. These processes were believed to occur at isolated chain units while the macroligand was accounted for by a set of independent complexing groups. Calculations involved overall concentrations of functional groups. Bjerrum's method and various modifications of this were widely applied: the complex formation process was thought of as successive addition of metal ions by independent functional groups of a macromolecule. Usually, the formation function, $\bar{n}$, the concentration of bound groups/total ion concentration, is equal to $f(K_i[L])$ was calculated and the number of bound functional groups per metal ion n, and stepwise formation constants, K_i, were determined by means of plotting $\bar{n}$ vs. $-\log [L]$. Stability constants were believed independent of the macroligand molecular weight [32].

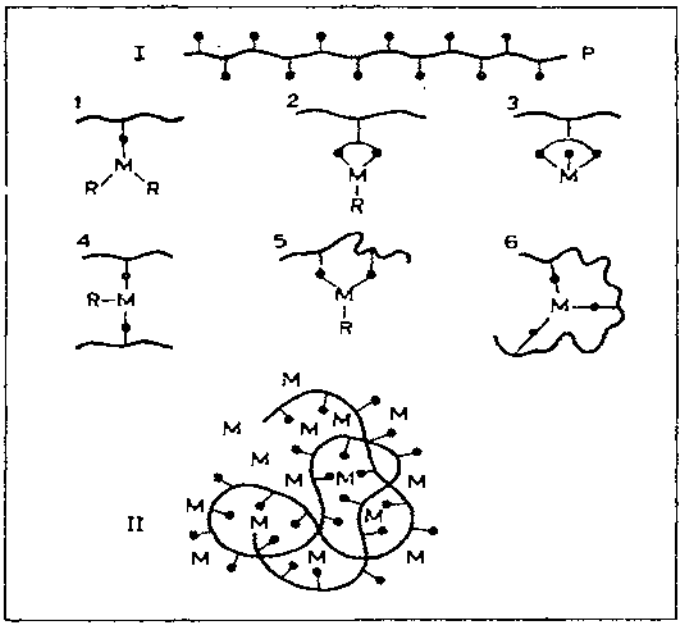


Fig. 6. Complex formation of polymer P in inner coordination nodes I and in the macrocomplex as a whole II.

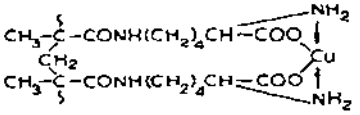
Tolmachev [33] puts forward an alternative method to deal with processes of complex formation involving macromolecules, which better conforms to the polymer nature of these macroligands. First consider the individual functional groups to bind metal ions and form "inner coordination nodes". One can then think of total complex formation as the process resulting in inner coordination nodes on the one hand and in the macrocomplex as a whole on the other, Fig. 6. Hence two sets of complex formation constants follow:

(i) constants, K_m characteristic of the free energy of the formation of coordination nodes; stepwise complex formation constants give series which differ for different nodes belonging to the same macromolecule and should depend on the macromolecular weight;

(ii) constants, K_p, characteristic of the free energy of the macrocomplex formation as a whole, describing stepwise addition of coordination nodes to a macromolecule. Such an approach has been used in the study of protein molecules [34,35].

Thus in general macromolecular complex formation represents a complicated process of branching off character. In real cases, however, some of the coordination nodes are predominant. With high local spatial concentrations of functional groups offered by a macromolecule the formation of ML_2 nodes is favoured. Irrespective of the way of analyzing macromolecule complex formation, this so called "concentration effect" appears to represent just one

among those contributing to the influence of the macromolecular nature of the ligand on the reactivity of functional groups [6]. Morawetz [36] reports the concentration effect to operate in Cu^{2+} with polymethacryllisine. Owing to this effect the polymer exhibits complexing ability at relatively low p*H* values, under which conditions no complex formation occurs in solutions of the low-molecular weight model. To realize this phenomenon, each of the acryllisine polymer molecules should be regarded as a volume of polyamino-acid solution forming complexes in spite of the build up of 22-membered rings thereupon (17,18).



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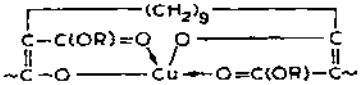


(18)

With Cu^{2+} and polydiethyldecanoate, the possibility of complex formation giving rise to interchain soluble complexes via building up of 15-membered rings shows, again that there is no limitation in the size of coordination center rings, which is a limitation characteristic of low-molecular weight complexes comprising 5 to 6 atoms (concentration effect) [24].

Macromolecular complex formation represents a still more involved process in the case of the mutual influence of functional groups. This type of interaction includes those of electronic origin (induction effect, conjugation), field effect, dispersion interactions, hydrogen bonding, solvation and supermolecular structure formation. Quite a number of these can not be expressed in a clearcut quantitative way so far, nor can their contribution to equilibrium constants characteristic of macromolecular complex formation be written explicitly. Therefore the only realistic way of describing polymeric complexing systems involves usage of averaged values (see p. 203).

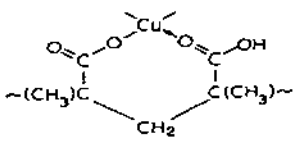
There is much information concerning the electrostatic effect in complex formation. A free energy change caused by the deprotonation of the polymer anion of, say, polymethacrylic acid, results in a shift of ionization equilibrium due to changes in activity coefficients, to the formation of ion pairs or to the specific binding of counterions. In the simplest case the electrostatic effect with polymeric acrylic acids or polymeric nitrogen-containing bases originates from an excess attraction (or repulsion) of complexing groups. Leite and coworkers [37,38] describe the formation of mononuclear or binuclear copper complexes in solutions of polymethacrylic acid as determined by the degree of neutralization in terms of the ratio:

$$f = \frac{\text{equivalent concentration of ionized polyacid}}{\text{equivalent concentration of } Cu^{2+}}$$

With low charge density on polymethacrylic acid (f value equal to 1.3) binuclear complexes of D_{4h} symmetry with two polymer ligands arranged to give rise to the four-fold axis occur, as indicated by spectral and static magnetism

data. With increasing polyelectrolyte charge up to an *f* value of 3.3, binuclear complexes undergo dissociation to give rise to mononuclear species. In the latter, negatively charged ligands form a distorted octahedron around the central ion. Polyglutamic acid is reported by Japanese workers [39] to exhibit a similar dependence of complex formation process on the degree of neutralization of the macromolecular ligand.

Polymer microstructure dependence of the reaction rate may be regarded as indication of the so-called "configuration effect". The effect is similar to that operating in the formation of diastereoisomers with low-molecular weight organic compounds. Complex formation reactions of polyacrylic and polymethacrylic acids have been most studied. At the same time, reliable methods exist for producing these acids in isomer forms (*iso-* and *syndio-*). Geuskens and co-workers [40] report different pathways for the reactions of isotactic and syndiotactic polymethacrylic acids (19,20).



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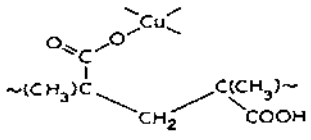


(20)

The isotactic acid exhibits higher reactivity compared to its syndiotactic isomer, and the rate of the complex formation in the former case is 1.5 times as high as in the latter, Fig. 7. The activation energy amounts to 6 and 7 kcal mol^{-1} respectively. In contrast, Crescenzi and co-workers [41—43] who studied the Cu^{2+}, Co^{2+}, Ni^{2+} and Mg^{2+} complex formation with *iso-* and *syndio-*polymethacrylic acids by an indirect method (Na^+ liberation) showed that the activity coefficient γ_{Na^+} vs. $R = [M^{2+}]/[Pol]$ varied negligibly in going from one isomer to the other, and only at small R values, Fig. 8.

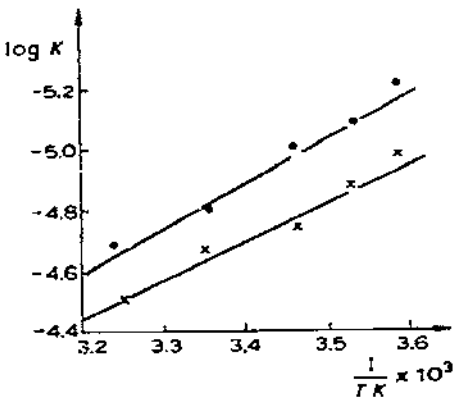


Fig. 7. Kinetic curves [40] of complex formation of *iso*-(1), and *syndio*-(2)-polymethacrylic acids with Cu^{+2}.

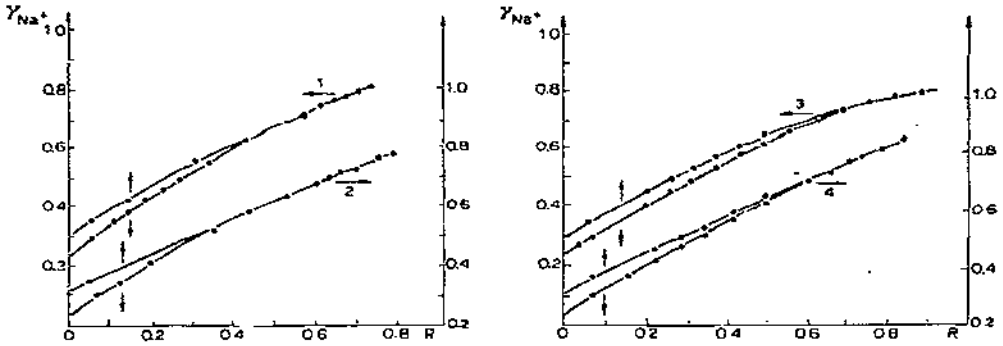


Fig. 8. Complex formation of Co^{+2}(1), Ni^{+2}(2), Mg^{+2}(3) and Cu^{+2}(4) with *iso*-(upper lines) and *syndio*-(lower lines) - polymethacrylic acids.

"Synthetic muscle models" provide the most striking examples illustrating the specific polymer nature of macromolecular ligands. This phenomenon finds no parallel at all in the chemistry of low-molecular weight complex compounds. Teyssie and co-workers [44] report strong chain contraction due to the formation of coordination centers (e.g. of the type shown in Fig. 9) in the binding of polyvinylamine to a complex with Cu^{2+}, Ni^{2+} or Zn^{2+} ions. This results in a four-fold or greater decrease in viscosity of solutions of polymer complexes.

"Reversibly contracting systems" are widely known [45, 46], these involve simultaneous complex formation and redox processes. Swollen and partly crosslinked fibers of polyvinyl alcohol (10% of polymer ligand and 90% of

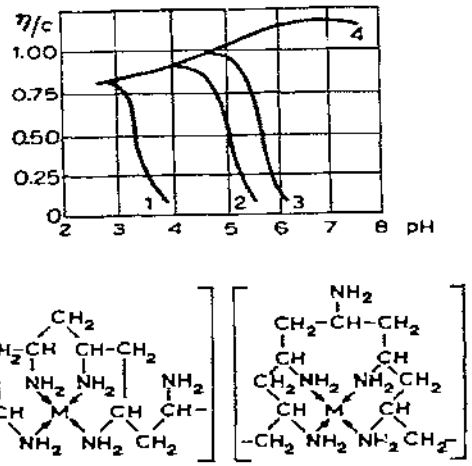
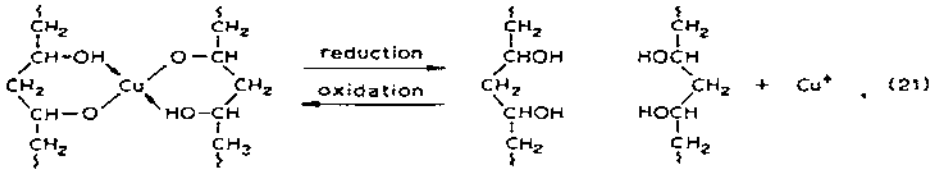


Fig. 9. The influence of complex formation with Cu^{+2}(1), Ni^{+2}(2) and Zn^{+2}(3) upon the viscosity of polyvinylamine solutions (4).

water content) react with copper ions to give greenish macromolecular complexes. The complex formation produces strong, dynamometer detectable



(21)

fiber contraction. Reduction (H_2/Pt) of the coordinated ion to Cu^+ results in a decomposition of the polymer complex characterized by concomitant discolouration of the mixture and by fiber elongation up to the initial size. On the contrary, oxidation (O_2/Pt) of the reduced system results in complex formation, colouring and fiber contraction (21). Recently Japanese workers [47] observed changes (decrease) in crystallinity, in the swelling index and in the solubility of polyvinyl alcohol film with complex formation involving Cu^{2+}. These changes resulted from orientation disordering of the polymer chains. On the other hand, the physical structure of the ligand, for example the extent of uniaxial tensile strain, strongly influences the process of complex formation with copper ions. Dunn [48] and Andrews and co-workers [49] claim the same to be true for nylon-6 films $\sim(CH_2)_5—CONH—(CH_2)_5—CONH—(CH_2)_5\sim$ in which case complex formation with transition metal ions finds ready response in mechanical properties, such as for instance tensile strength.

Recently, Kabanov and co-workers [50] have carried out an investigation on the interaction of copper ion and partially alkylated poly-4-vinylpyridine. These authors made use of ESR, visible spectroscopy, paramagnetic label, sedimentation rate analysis and viscosimetry techniques to show that the reaction under study followed a specific pathway when compared to the reaction of copper with a low-molecular weight analogue, 4-ethylpyridine. (i) Four-coordinated complexes, $CuPy_4^{2+}$, were formed predominantly irrespective of the ratio of Cu^{2+} ion to free pyridine group concentration in aqueous solution; (ii) the reaction proceeded with sufficiently high a rate so that stepwise development of the process, characteristic of interactions of low-molecular weight compounds, remained undetected; (iii) the reaction in solution appears to give rise to aggregates composed of a few macromolecules; these combined with copper ions in such a way that in the same complex pyridine ligand units belonging to various fragments of a number of macromolecules occurred; (iv) the reaction was considerably influenced by such factors as solution ionic strength and the degree of ligand alkylation (that is, by the content of charged groups). The polymer characteristics derive from a high local concentration of complexing groups in a coiled molecule, from the polyelectrolyte conformational state, from the electrostatic effect and unusual characteristics of the polymer hydration sheath.

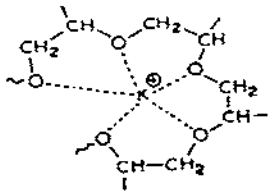
A notable reduction in the volume of the macromolecule was shown to occur on complex formation. In the case of poly-4-vinylpyridine the limiting

value of the intrinsic viscosity was twice as low as that observed in the presence of an adequate quantity of a divalent metal ion which cannot bind to the ligand. It is of interest, that in spite of copper exhibiting a pronounced ability to form four-coordinated complexes and hence for "cross-linking" macromolecular units together, no precipitation of polymer complex occurs even at high Cu^{2+} concentrations. This may be due to the twisting out of positively charged alkylated pyridine groups in the conformational rearrangement associated with the formation of tetrapyridine complexes. Accordingly the macromolecule surface acquires a positive charge which hinders further aggregation. Moreover it has been shown that the enthalpy change in Cu^{2+} polymer complex formation differs from that of the formation of the tetracomplex with 4-ethylpyridine ($-\Delta H = 10 \pm 1$ and 18 ± 2 kcal mol^{-1} respectively). This may originate from a lowering of coordination M . . . L bond energy due to the electrostatic repulsion of positively charged macromolecules. Seemingly, an increase in the acid dissociation constant of the pyridine group in the polymer is of the same origin [50].

Macromolecular ligands are known which can combine via complex formation with non-transition metal ions. Davydova, Plate and co-workers [51] report spectrophotometric data on the interaction of polyesters of polypropylene glycol and polyethylene glycol with salts of alkali metals (KNCS, NaNCS) and ammonium (NH_4NCS). Judging by the equilibrium constants for complex formation the polyesters possess low specificity towards the ions under investigation:

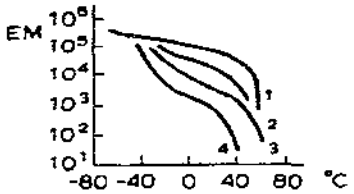
Ligand	$\log \beta_{K^+}$	$\log \beta_{Na^+}$	$\log \beta_{NH_4^+}$
Polypropylene glycol, mol. wt. 2000	1.3	1.3	1.6
Polyethylene glycol, mol. wt. 15000	3.0	2.0	2.6

The cooperative effect contributes to the complex formation of, for example, potassium with oxygen atoms of the polyester macromolecule in a macroligand globule. The same conclusion follows from data on coordination center structure in the potassium complex with polyethylene glycol [52] (22).



(22)

Cooperative solid phase interaction of polyethylene glycol monomer units with ions of potassium and rubidium (KI, KF, KCl, KBr, RbF, RbI) finds indirect support in a marked decrease in polymer crystallinity when in the presence of the corresponding salt, Fig. 10. The authors claim some 9 polymer units participate in bonding with potassium or rubidium ion [53].



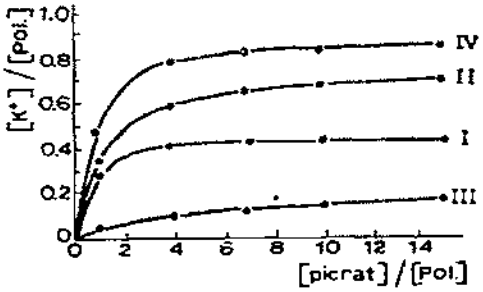
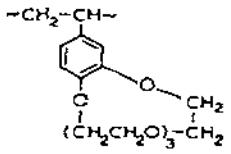


Fig. 10. The elasticity modules EM of polyethyleneglycol (1) versus content of KI [2—10%, 3—20% and 4—30% KI].

Fig. 11. The kinetics of complex formation of polyvinylmacrocyclic polyesters (23) I and (24) II(in comparison with (25) III and (26) IV) with K-ions; [ligand] = $7 \cdot 10^{-5}$ mol.

Recently, polyvinylmacrocyclic polyesters of the polyoxyethylene type were reported to produce complexes with alkali metal ions. Smid and coworkers [54] have carried out an investigation on complex formation with polymer macrocycles (23) and (24). These are similar to the so-called crown-



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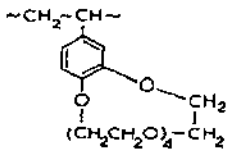


(24)

compounds discussed by Pedersen [55], (25 and 26). The complexing activity of the polyesters under discussion, as determined by the technique of picrate extraction [55], and expressed in % M^+ extracted by the ligands (23) or (24) from 1 : 1 H_2O : CH_2Cl_2 and 0.1 *N* M^+ is considerably higher, especially for (23), than for the monomeric (25) and (26):

Metal ion	(23)	(25)	(24)	(26)
Li^+	10.0	1	6.3	1.01
Na^+	24.7	10.6	20.7	13.1
K^+	85.2	22.3	90.2	85.6
Rb^+	83.7	13.0	84.2	74.0
Cs^+	68.8	3.5	87.9	71.0

The authors believe the extra polyligand complexing activity results from the cooperative interaction between two adjacent groups in the polymer, Fig. 11.

The cooperative effect or the so-called "chain effect" can manifest itself in a variety of ways. Recently, a considerable decrease in donor activity of the

—C=O group when in a macromolecular ligand (polymethylmethacrylate, polyvinylacetate, polyacrylonitrile) was observed upon complex formation with vanadium salts. The decrease results from partial delocalization of oxygen unshared electron pairs over the macromolecular chain, which reduces the degree of electron transfer to transition metal vacant *d*-orbitals [56].

Reactions between metal ions and proteins or nucleic acids offer examples of ligand macromolecular character influencing complex formation in the case of naturally occurring macromolecular complexes.

When isolated from various biological objects, nucleic acids incorporate certain amounts of one or a number of metals. Walker and Vallee [57] report samples of DNA and RNA to contain chromium, nickel, iron, manganese, zinc, etc. Metals coordinatively bound to nucleic acids are difficult to remove even when using such strong complexing agents as ethylenediaminetetraacetic acid or 8-hydroxyquinoline. Metal ions are suggested to account for the binding of nucleic acids to protein [58], to be essential to the functioning and structure of nucleoproteins [59,60], and to influence protein synthesis and hereditary information transfer [57]. Fe^{3+} ions appear paramount in DNA functioning; these ions participate in the formation of bonds between separate chains and provide control of the denaturation processes [61]. DNA biosynthesis itself involves redox transformations of iron and copper ions; oxidation of metal ions causes weakening of complementary pair linkage between DNA bases, whereas reduction results in stabilization of bystrand DNA conformation [62].

Walker et al. [63] draw the conclusion that all of the first transition series ions effect stabilization of nucleic acid structure via metal-to-base coordination bonding. This bonding is strong enough to resist elevated temperatures and urea denaturation.

The polymeric nature of DNA and RNA strongly affects the properties of the transition metal complexes they form. As a rule, bonding to a metal causes reversible changes in structure and properties of the nucleic acids [64]. As early as 1952, Katz [65] has shown that interaction with mercury ions causes the dimensions of DNA molecules to decrease; when treated with mercury binding reagents, the molecules regain their initial size. More recently, quite a number of authors [66—69], have substantiated the reaction of DNA with Fe^{3+}, Hg^{2+}, Ag^{+} ions to be reversible by applying methods sensitive to the shape and size of macromolecules (specific viscosity, sedimentation rate, light scattering, rotary dispersion), or sensitive to the presence and relative position of chromophore groups on macromolecular chains (spectral data).

In many cases the stabilities of nucleic acid complexes are in satisfactory agreement with those predicted from data on complex formation with low-molecular weight analogues, provided the cited effects characteristic of interactions with macromolecules are taken into account. Thus, the effect of secondary structures on the reactivity of complexing functional groups in proteins (COOH, NH_2, NH, SH, OH, etc.) appears to consist in "concentra-

ting" these groups (concentration effect) via specific coiling of polypeptide chains [70]. Data on a complex protein coordination compound, cytochrome-oxidase (2 Cu^{2+} and 2 Fe^{2+} per enzyme molecule) show copper ions to give rise to a spin—spin exchange interaction, which suggests these ions fall close together [71]. With lactase (4 Cu^{2+} per enzyme molecule), only 50% of the expected quantity of Cu^{2+}-content has been detected by ESR technique; an observed reduction in unpaired electron density on copper nuclei appears to be related to interactions between *d*-electrons of the ions [71]. Purmall et al. [72] claim binuclear character for the catalase active center which contains four iron—porphyrin groups. In all of these cases, equally charged metal ions are likely to approach each other on account of complex formation with negatively charged ligands causing a decrease in ion effective charge, and binding of metals via anion bridges. The examples cited demonstrate effects of concentration and electrostatic factors on the complex formation process and characteristics of the resulting complexes with macromolecular ligands.

Naturally occurring polymers, DNA and RNA, as well as synthetic models of these, polyadenylic and polyuridylic acids [69], combine with ions of 3*d* and 4*f* transition series to give rise to coordination centers of uniform or mixed ligand composition, both of which may even belong to the same polymer chain [73]. Stern and Steinberg [74] believe lanthanide nucleates (via phosphatic groups), of which complexes of DNA with lanthanum, neodymium, praseodymium, samarium and yttrium of 3 : 1 composition have been reported, build up the macromolecular coil comprising a two-chain helix centered at metal ion, or are otherwise involved in the cross-linking of DNA macromolecules. Coordination center composition has also been considered by others [75—77]. The formation of nucleates with transition metal to RNA or DNA ratio equal to 2 : 1, 1 : 1 or even less [78,79] can be accounted for by the ability of these polyfunctional molecules to participate in complex formation via various functional groups on the chain, that is via phosphatic groups (Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cr^{3+}), amino groups (Cu^{2+}, Pb^{2+}, Fe^{3+}, Hg^{2+}, Ag^{+}) or enol groups; it can also be attributed to complex formation involving low-molecular weight ligands present in the reaction mixture.

Yatsimirskii and Kriss [80] suggest metal ions, particularly those of transition series, are able to form coordination bonds with a variety of functional groups on RNA or DNA macromolecules, thus giving rise to various coordination centers with individual stability constants. Therefore experimental constants commonly represent averaged characteristics.

Even from the few examples cited one can see that the spatial and electrostatic cross-influence of chain fragments contribute dominantly to specific polymer effects on the reactivity of complexing macromolecules. The effect of ligand macromolecular character on the efficiency of complex formation can be seen in almost all of the scientific publications concerning soluble macroligands, insoluble ligands, and also naturally occurring macromolecules. Therefore any investigation of complex formation with macromolecules of any type should take into account the polymeric state of the reagents.

E. CHEMICAL TRANSFORMATIONS OF COMPLEXES WITH MACROMOLECULAR LIGANDS

Usually the reactivity of macromolecules is considered from the viewpoint of the types, rates and thermodynamics of chemical transformations which the functional groups or the macromolecule as a whole undergo. In this section the reactivity of complexes with macromolecular ligands is discussed in connection with the direction of reactions proceeding with, or in the presence of, macromolecules of a given type.

One is often interested in the catalytic activity of complex compounds. Polymer complexes as catalytic agents in inorganic and organic reactions offer obvious advantages over low-molecular weight compounds owing (i) to the ready separation and regeneration of catalyst and, (ii), of primary importance, because the former give rise to constant, if not low, metal ion concentrations in solution in equilibrium with insoluble polymer complex (25). Macromolec-

$$-[fM] \rightleftarrows -[f^{n-1}] + [M^{n+}] \qquad (25)$$

ular ligand complexes like analogous low-molecular weight species may behave as catalysts in the oxidation of ascorbic acid. In this reaction, tetrapyridine complexes of Cu^{2+} with poly-4-vinylpyridine have been shown to produce catalytic effects 2 to 3 orders of magnitude stronger than those of the copper complex with the low-molecular weight, 4-ethylpyridine, or those of Cu^{2+} ions as such. The specific character of macromolecular complex formation may also be responsible for the higher catalytic activity of copper ions bound to a complex with a macromolecular ligand [81].

Complexes of polymeric hydroxamic acids, poly-β-ketoesters and poly-β-diketones have also been reported to possess ascorbooxidase activity [82,83]. In addition, catalytic activity towards hydrogen peroxide decomposition is characteristic of macromolecular ligand complexes; according to literature data, complexes with polyhydroxamic acids, polyketoesters, polydiketones and polymeric picolinic acids [84,85] possess catalase action.

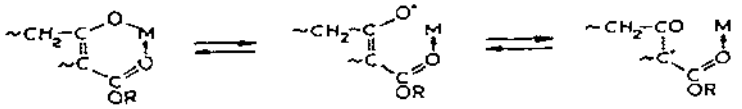
Data on the oxygen oxidation of a variety of organic compounds (of many different hydrocarbons, of aldehydes and of acetals of these, of methacrolein, of furol etc.) in the presence of polymeric complexes have been reported for the following types of coordinated macromolecular ligands: polyphthalocyanines [86], polyaminestyrene-*N*,*N*-diacetic acid and polyformaldehydesalicylates [87], polyhydroxamic acids [82] and many others. Coordinated ions follow the ordinary activity series in all of the cases [88]. Many of the papers cited report higher reactivity of macromolecular complexes compared to that of low-molecular weight analogues.

Complexes with macromolecular ligands of β-ketoester and β-diketonic types also prove active towards transesterification of esters [89]. Again in this case the catalytic activity of coordinated ions follows the low-molecular weight complex stability series of Irving—Williams [90].

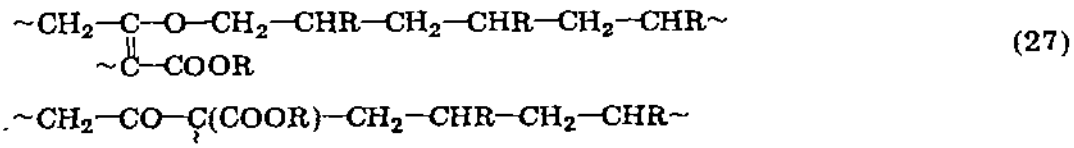
Of particular interest is the activity of complexes with macromolecular

ligands of various types towards the initiation of polymerization of vinyl monomers. Literature data exist for the catalytic effect of low-molecular weight compounds: of acetylacetonates on polymerization of butadiene [91, 92], of trifluoroacetylacetonates on polymerization of methylmethacrylate [93,94], of substituted β-diketonates on polymerization of methylmethacrylate and other monomers [95], and of oligomeric ethylene amines on polymerization of a number of monomers [96]. These processes result in polymers with (or sometimes without) a corresponding ligand molecule linked to the head of the growing chain, which has no pronounced effect on the structure and properties of the reaction products.

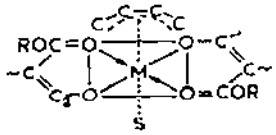
Of far greater concern is the case with macromolecular ligands, e.g. of poly-β-ketoester type, participating in polymerization [97]. In addition to their initiation activity these produce graft polymers incorporating chains of monomer. Graft copolymers of styrene or butadiene and polyketoester (with coordinated metal removed) result from homolytic cleavage of ligand-to-metal bond*:


(26)

with subsequent radical polymerization of vinyl monomer via O- or C- radical:


(27)

Polymer complexes of manganese and cobalt which are characterized by relatively low stability ($\log \beta_2 = 7.1$–7.3) exert the strongest initiating influence on the process of vinyl monomer polymerization. The existence of unsaturated coordination centers or "defect" character in the macromolecular complex chains appears to favour additional coordination of vinyl monomer by central metal atom [98] (28).


(28)

This results in a weakening of ligand-to-metal bonding and consequently favours homolytic cleavage according to (28). Japanese authors also suggest preliminary binding of the monomers to influence the acetylacetonate decomposition step of the polymerization process [99].

The ability of a coordinatively unsaturated metal atom incorporated in a

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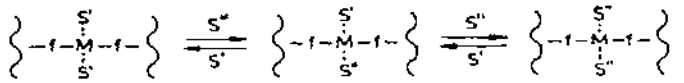
* According to Bamford [94] for the case of low-molecular weight compounds.

complex with a macromolecular ligand to take advantage of coordinative vacancies appears to be essential to the so-called ligand exchange (29).



(29)

Ni^{2+} complexes of ion-exchangers containing, say, iminodiacetic acid residues [100] have been used in separating amines [101], phenols [102], and also purine and pyrimidine bases, unsaturated hydrocarbons, monosaccharides, peptide aminoacids, humic acids and other naturally occurring compounds [103]. Rogozhin and Dovankov [104—106] report dissymmetric ion-exchangers containing optically active α-aminoacid groups. Metal complexes (Cu^{2+}, Ni^{2+}, Zn^{2+}) of these sorbents allow quantitative separation of optical isomers. The order of isomer elution is related to the stability of the complexes these form with the polymeric stationary ligand; therefore this technique can be applied to studying kinetically labile mixed complexes.

Quite recently data have become available using polymer complexes as catalysts in hydrogenation and hydroformylation of unsaturated compounds [107—111]. Thus, according to Robinson, Paulik et al. [112,113], the triphenylphosphine complex of rhodium carbonyl on a solid carrier can be used to effect olefin hydroformylation under rather mild conditions. Polymer complexes of this type represent catalysts of high stability and high reactivity giving rise to reaction products of the same normal-to-branched aldehyde ratio as that resulting from reactions in the presence of low-molecular weight complexes [114].

Other authors fixed the triphenylphosphine—rhodium carbonyl complex in a polymer matrix containing polystyrene incorporating nitrogen-, phosphorus- or sulfur- containing groups. With these polymeric complexes, hydroformylation of hexene-1 was characterized by the same yields, selectivities and activities as those observed with the low-molecular weight complexes, $HRh(CO)(PPh_3)_3$ and $ClRh(CO)(PPh_3)_2$. In the authors' opinion, polymeric complexes of this type may be used in hydroformylation in the gas phase [115, 116]. Moffit reports [117] the partial decomposition of a cobalt polymer complex with poly-2-vinylpyridine as base polymer according to the equation

$$[\text{Polymer} \times HCo(CO)_4] \rightleftarrows [\text{Polymer}] + [HCo(CO)_4]$$

in hydroformylation in the liquid phase. The reverse reaction, that is decarbonylation of aldehydes giving rise to olefins, occurs in the presence of polymer complexes of platinum metals or of manganese [118, 119].

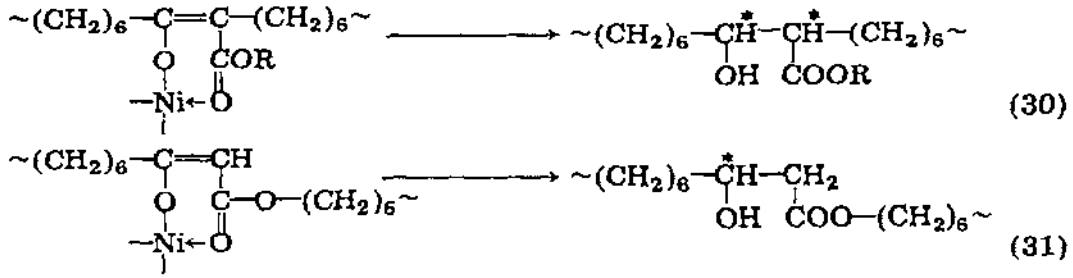
One more striking example of chemical transformations of macromolecular complexes is offered by the catalytic hydrogenation of nickel complexes with macromolecular ligands of the β-dicarbonyl type, which results in the corresponding polyketoesters [120—123]. Under asymmetric conditions (in the presence of *L*-glutamic acid) hydrogenation gives rise to the corresponding optically active reaction products, Table IV (30,31). Data by Izumi et al.

TABLE 4

Hydrogenation of nickel complexes with macromolecular ligands of the β-ketoester type (30,31) and with low-molecular weight analogues (H_2 = 100 atm., 100°, 12 h)

Complex	The extent of hydrogenation	$[\alpha]_{589}^{20}$ (deg.)
Nickel polydiethylazelate, (30)	100	0.0
Nickel polydiethylazelate, (30)	95	+1.2[a]
Nickel acetoacetate	95	0.0
Nickel acetoacetate	85	−2.0[a]
Nickel polyoxaloacetate, (31)	90	0.0
Nickel polyoxaloacetate, (31)	90	+8.6[a]
Nickel oxaloacetate	95	0.0
Nickel oxaloacetate	95	−1.3[a]

[a] In the presence of *L*-glutamic acid



(30)

(31)

[124] on asymmetric hydrogenation of Ni^{2+} complexes with related low-molecular weight compounds, namely of nickel methylacetoacetate and of nickel acetylacetonate, substantiate the above results. To all appearances, the reaction of asymmetric hydrogenation of complexes with macromolecular ligands can be extended to many other types of metals and of complexing groups, which would provide a novel synthetic route to optically active polymers.

Polymer transition metal complexes can simulate metal-containing enzymes. A model of catalase has been studied by Kabanov and co-workers [125, 126] with Cu^{2+} complexes of polyacrylic or polymethacrylic acids; these decompose hydrogen peroxide in the presence of ethylenediamine or other aliphatic amines with the rate constant equal to $2 \cdot 10^5$ mol^{-1} sec^{-1} (action by catalase on H_2O_2 decomposition is characterized by the rate constant $6 \cdot 10^7$ mol^{-1} sec^{-1}). In spite of differences in structure of active center, the decomposition mechanism is the same with catalase and with the polymer complex. Similarly to catalase, model complexes exhibit high selectivity towards H_2O_2 while being practically inactive towards other peroxide compounds.

In contrast to various low-molecular weight complexes of Fe^{3+}, Cu^{2+} and other transition metals used to simulate catalase action, polymer complex

induced decomposition of H_2O_2 represents a stepwise reaction involving two molecules of H_2O_2 rather than a radical process; the formation of a peroxo-complex with a catalyst active center was shown to occur in this case. The process activation energy amounts to 2.3 kcal mol^{-1} with the polymer complex and to 1.7–2.5 kcal mol^{-1} with catalase which indicates the transition states to be similar in both of the cases.

The ability of metal ions in macromolecules, remaining unsaturated with respect to ligands, to undergo redox transformations was taken advantage of in the development of electron—ion exchangers characterized by redox potential variation over a considerable range. Polymeric oxidizers and reducers have been obtained which possess redox potentials different from those inherent in corresponding solvated ions [127]. Metal-containing electron—ion exchangers have been used in preparing polymer reagents able to remove oxygen from solutions [128]. Recently, Japanese authors [129] have studied electron-transfer reactions involving mixed ligand complexes of polyvinylpyridine or polyvinylchloride with ethylenediamine. A clear-cut distinction between polymer and monomer complexes was shown to exist in the kinetic and thermodynamic characteristics of the reaction; the polymer complexes possessing lower reactivity and giving rise to higher ΔH and ΔS for the reaction compared with low-molecular weight complexes.

Undoubtedly, chemical transformations of complexes with macromolecular ligands of any type are not limited to asymmetric hydrogenation, catalytic activity and to simulating enzyme systems. Coordinated macromolecules can participate in practically any reaction which low-molecular weight complexes are known to undergo, however, one should keep in mind all of the specific features cited above, characteristic of the structure and properties of the former.

The problem of whether complexes with macromolecular ligands possess higher activity, for example, as catalysts in the above reactions, compared to their low-molecular weight analogues, and if so, wherein lies the origin of this higher reactivity, is not unambiguously solved. Some authors [88,97,125] attribute the higher catalytic activity of polymer complex compounds of various types and in various reactions to defect structure of coordination centers, to the unsaturated character of these and to their ability to coordinate substrate molecules. Others attribute the high catalytic activity of polymer complexes to the so-called cooperative effects [130].

Further detailed study in this field is needed to remove such ambiguities.

There is no doubt that this field, which has been under active investigation in recent years, opens the way for discoveries and constitutes an important part of the current chemistry of high-molecular weight, bio-inorganic and coordination compounds.

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