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POLYMERIC CO-ORDINATION COMPOUNDS

I. Haiduc

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INTRODUCTION

The widespread practical application of polymeric compounds and theoretical aspects of polymer chemistry have governed the development of research in this field during recent years. At the present time a great deal of attention is being paid to inorganic and organo-elementary polymers.

Application of the concept of polymerism to inorganic chemistry is one of the factors which has recently determined progress in this branch of chemistry and influenced our ideas on the relation between organic and inorganic chemistry. Whereas in 1952 it was considered[1] that "organic chemistry is the science of a more highly organised form of matter than is inorganic chemistry" and "inorganic chemistry is mainly concerned with relatively simple molecules", this would not be correct today. Many structures known only in organic chemistry became known also in inorganic molecules, for example cyclic[2,3] and macromolecular[2,4-14] inorganic polymers, etc. Determination of the molecular weight and study of the structure of inorganic compounds, such as $PdCl_2$, $CuBr_2$, $Be(CH_3)_2$, has shown that they are often polymers. Many salts do not have a discrete structure (do not consist of independent ions or molecules), but are polymers having covalent or co-ordinate bonds more or less ionic in character.

The inorganic polymers to which we had been accustomed were mainly derivatives of non-metals, the macromolecular skeleton of which was formed by normal covalent bonds. Published reviews[2,4-8] with a few exceptions[4,10] consider only these inorganic polymers. However, the following considerations show that it is also possible to obtain polymers in which the molecular skeleton is formed by co-ordinate links.

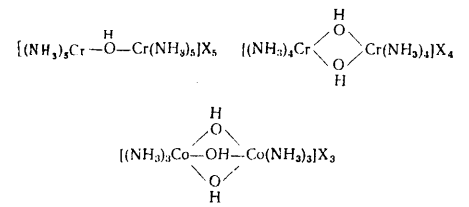
Since it is immaterial whether the two electrons of a covalent bond originate from the same atom or from two different atoms, a co-ordinate link does not differ fundamentally from a "normal covalent bond".[15,16] Because of the displacement of the electrons, the formation of a co-ordinate link involves the appearance of electric charges (whence the name "semipolar bond"). For example

covalent bond BN: $R_2B—NR_2$,

co-ordinate link BN: $R_3B \leftarrow NR_3$ or $R_3\bar{B}—\overset{+}{N}R_3$.

Consequently, the existence of high polymers formed by normal covalent bonds leads to the conclusion that such polymers can be formed also by co-ordinate links[17].

As early as the classical period of the chemistry of complex compounds, polynuclear complexes were synthesised in which the co-ordinate octahedra were joined by common corners, edges, or faces: *i.e.* in which one, two, or three bridging bonds are formed between the central atoms, for example



It can be concluded that several co-ordination centres can be joined by such bridging bonds. For a long time the chemistry of complex compounds was unable to determine whether it is possible to obtain polymers of high molecular weight based on this principle.

Co-ordinate links increase the number of bonds between atoms by involving a larger number of electrons and unfilled orbitals[16]. Metal atoms form co-ordinate donor–acceptor links, the number of bonds formed exceeding the normal valency due to vacant orbitals. Non-metals utilise their lone pairs of electrons to form bridges. Such groups as $-\bar{O}H$, $-\bar{N}H_2$, $-\bar{S}H$, $-\bar{C}l|$, $-\bar{B}r|$, etc., are able to form bridges, but the NH_3 molecule, which possesses only one lone pair of electrons, cannot form more than one bond, and can act only as a terminal group in a polymer.

X-Ray investigation has shown the polymeric nature of many "simple" and complex inorganic compounds[4,7,11-14], in which polymerisation is due to the formation of co-ordinate links.

Structures of both low and high molecular weight, such as palladium chloride $PdCl_2$, can be formed through co-ordinate links.

A more important concept than valency in the chemistry of co-ordination polymers is that of the "bondability" (*Bindigkeit, svyaznost'*) of an atom, *i.e.* the number of bonds which it forms with other atoms. In practice this is identical with the co-ordination number (C.N.).

Schmitz-Dumont[18,19] uses the term "high-polymer co-ordination compounds" (*hochpolymere Koordinationsverbindungen*) for these compounds, and Schwarzenbach[20] the term "high-polynuclear complexes" (*Hochpolynucleare*). In this review we will use the term "co-ordination polymers" for polymers of low and high molecular weight. We will count as *co-ordination polymers all polymeric compounds containing atoms forming a greater number of bonds than corresponds to the valency of given element.* This class includes both polymers formed by donor–acceptor bonds and electron-deficient polymers with many-centre bonds. In all cases polymerisation results from the tendency of elements to make maximum use of their valency electrons and vacant orbitals to form covalent, dative, co-ordinate, or many-centre bonds (for types of chemical bonds, see the review by Syrkin[16]). Polymers of this type can be formed by boron, transition metals, and elements of the main subgroups whose valency is less than their co-ordination number. All these elements tend to form bonds in excess of their valency: polymerisation provides one possible method of implementing this tendency.

Polymeric compounds of elements of co-ordination number equal to their valency, *e.g.* Mo, W, Te (C.N. = valency = = 6) cannot be regarded as co-ordination polymers. Condensed oxygen compounds of these elements constitute the class of isopoly compounds, which are ordinary covalent polymers.

Co-ordination polymers have formed the subject of two reviews[10,19]; a third[21] is known to the present writer only through *Chemical Abstracts*.

Here we will consider various aspects of the chemistry and the structure of co-ordination polymers, and will attempt to incorporate these compounds in a general scheme of inorganic polymers. The number of known co-ordination polymers is still small; many opportunities exist for preparing new types of co-ordination polymers. In the present work, therefore, we will examine, besides the work in the

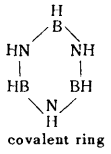
literature, some as yet unused methods, where existing knowledge indicates some promise of development in this field.

I. CLASSIFICATION OF INORGANIC POLYMERS

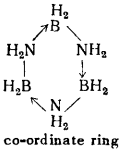
In order to assess the status of co-ordination polymers in the chemistry of macromolecular compounds we must consider the classification of inorganic polymers. Berlin and Parini[5,6] divide all polymers into (*a*) organic, (*b*) organo-elementary, and (*c*) inorganic, depending on the constitution of the main chain. Organo-elementary polymers contain other elements besides carbon (B, Si, Ge, P, As, Sb, etc., metals) in the chain; inorganic polymers contain no carbon in the main chain. Both organo-elementary co-ordination (chelate) polymers and purely inorganic co-ordination polymers are known.

Published reviews[5-8,10] make no distinction between polymers of low and of high molecular weight. The term "macromolecule" often refers to trimers and tetramers, most of which are cyclic compounds. Cyclic inorganic compounds possess definite peculiarities[3] and are therefore distinct from polymers of high molecular weight.

According to the present reviewer's classification[2,3], monocyclic compounds are divided into — (*a*) *homocyclic*, the ring of which is formed by atoms all of the same kind, *e.g.* S_8,[22] $(AsCH_3)_5$,[23] $(PCH_3)_5$,[24] etc.; (*b*) *pseudoheterocyclic* or *alternant*, in which the ring is formed by the alternation of two elements A and B, for example,



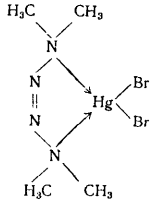
covalent ring



co-ordinate ring

(*c*) *true heterocyclic* compounds, such as S_7NH,[25] $R_6Si_3O_2NH$,[26] etc.

Cyclic co-ordination polymers consist almost exclusively of alternant rings, in which donor and acceptor atoms alternate. Very few examples are known of true heterocyclic compounds containing co-ordinate links, an example being the complex of tetramethyltetra-azen with mercuric bromide[27]:

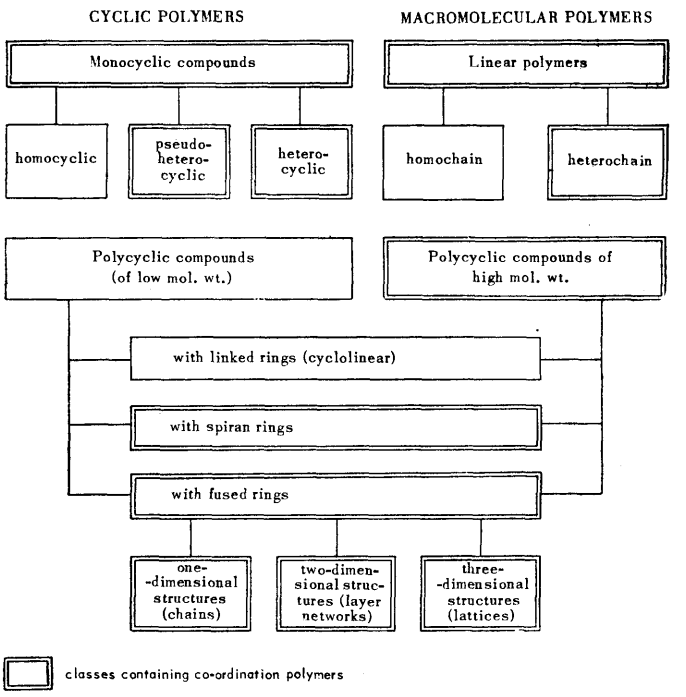


The following classification is suggested for inorganic polymers of high molecular weight — (*a*) homochain polymers and (*b*) heterochain polymers[2,4,28]. All co-ordination polymers, of course, are heterochain.

Table 1 gives a scheme for the classification of inorganic polymers.

Co-ordination polymers can be classified stereochemically according to the structural unit of the polymer — (*a*) polymers having tetrahedral structural units (C.N. 4), (*b*) polymers having square planar structural units (C.N. 4), (*c*) polymers having octahedral structural units (C.N. 6), (*d*) polymers having cubic structural units (C.N. 8), and (*e*) polymers having different structural units (different co-ordination numbers in the structure).

TABLE 1. Classification of inorganic polymers.



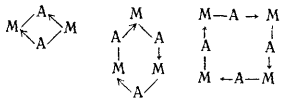
II. CO-ORDINATION POLYMERS OF LOW MOLECULAR WEIGHT

In this section we shall examine compounds having a low degree of polymerisation. This class includes cyclic co-ordination compounds (consisting of tetrahedral structural units) and several polymers containing heavy elements (their molecules being made up of octahedral structural units).

1. CYCLIC CO-ORDINATION POLYMERS WITH CO-ORDINATION NUMBER 4

When a compound contains both donor and acceptor elements in the molecule, polymerisation can occur by means of co-ordinate links, if other molecules which can take part in co-ordination are absent. The polymers of low degree of polymerisation (dimers, trimers, tetramers, hexamers) which are formed are usually cyclic compounds. If M is an

acceptor, and A a donor, MA molecules can polymerise by means of co-ordinate links:



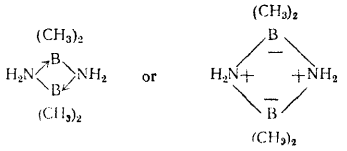
Cyclic compounds of this type are known in which M = B, Al, Ga, In, etc. If M has C.N. = 4, the cyclic polymers consist of tetrahedral structural units joined at the corners to form a ring.

The acceptor atom M is situated at the centre of the tetrahedron and is in a hybrid sp^3 state.

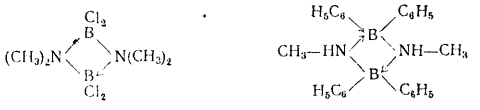
Compounds of boron. Trimethylboron forms with ammonia a compound $(CH_3)_3B.NH_3$, in which the free pair of electrons on the nitrogen and a vacant orbital in the boron form a co-ordinate (or semipolar) bond[29]:

$$(CH_3)_3B \leftarrow NH_3 \quad \text{or} \quad (CH_3)_3\bar{B}-\overset{+}{N}H_3.$$

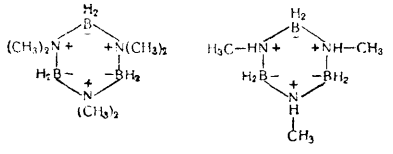
Thermal decomposition of this compound involves the evolution of methane and the formation of $(CH_3)_2BNH_2$, which is a cyclic dimer[30]:



Its isomer[31] $[(CH_3)_2NBH_2]_2$ is also a dimer. The same cyclobutane type of structure occurs[32] in the compounds $[(CH_3)_2NBCl_2]_2$ and[33] $[CH_3NHB(C_6H_5)_2]_2$ as shown by molecular weight and infra-red spectral data:

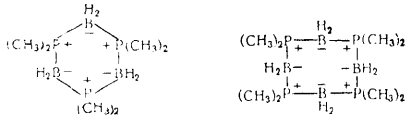


The compound $[(CH_3)_2NBH_2]_3$, obtained[34] by heating the corresponding dimer $[(CH_3)_2NBH_2]_2$, contains a six-membered ring. X-Ray examination of the trimer[35] showed that the B_3N_3 ring has the chair form, corresponding to its "saturated nature". A cyclic trimer is also known[36] having the composition $[NH(CH_3).BH_2]_3$:



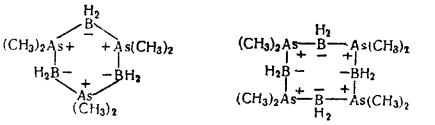
All these compounds evolve methane and are converted into borazole derivatives on being heated.

Burg and Wagner[37,38] prepared compounds in which phosphorus was the donor. They synthesised the cyclic compounds $[(CH_3)_2PBH_2]_3$ and $[(CH_3)_2PBH_2]_4$:



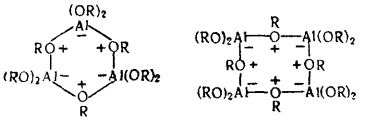
The cyclic structure of the trimer was confirmed by Hamilton[39] using X-rays. These compounds possess remarkable thermal stability: it has been established[40] by mass-spectroscopy that thermal decomposition of the trimer begins only at 360°, when hydrogen and methane are evolved. Very stable compounds having the composition $[(CF_3)_2PBH_2]_3$ and $[(CF_3)_2PBH_2]_4$ were synthesised[41] by reaction between $(CF_3)_2PF$ and B_2H_6. The compounds $[(C_6H_5)_2PBH_2]_3$, $[(C_5H_{10})_2PBH_2]_3$, $[(C_5H_{11})_2PBH_2]_3$, and $[(C_6H_{11})_2PBH_2]_3$ have been patented as dielectrics[42].

$(CH_3)_2AsH.BH_3$ yielded on heating cyclic trimers and tetramers[43]:



The stability of the co-ordinated boron rings decreases in the order N > P > As.

Compounds of elements of Group III (Al, In, Ga). In 1932 Ulich and Nespital[44] established that aluminium alkoxides $Al(OR)_3$ occurs as polymers in benzene solution. They showed that the solution contains co-ordinated cyclic trimers and tetramers:

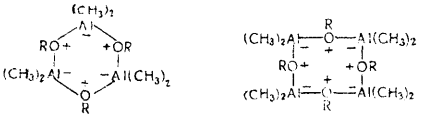


Later Mehrotra[45] studied a series of aluminium alkoxides, and showed that they were all polymeric (tetramers). Bradley, however, considers[46] that the degree of polymerisation of 4 is only apparent, and results from the presence of a dimer (C.N. 4) and an octamer (C.N. 6) in the solution.

In compounds of the type AlX_3 the aluminium atom is co-ordinatively unsaturated, having an unoccupied p orbital. In an oxygen-containing solvent, such as R_2O, the unshared electron pairs of the solvent molecule form a co-ordinate link with the aluminium atom, and the compound is monomeric owing to the formation of solvates. In benzene or other inert solvent such solvation is impossible, and co-ordination polymerisation provides the only opportunity for the aluminium to utilise all its valency orbitals.

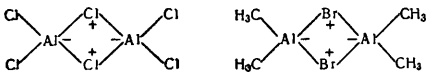
The apparent co-ordination number of aluminium in the compounds $Al(OR)_3$ is 3; on polymerisation, the co-ordination number in the cyclic molecules is obviously 4. This is typical of co-ordination polymers: *the actual co-ordination number is greater than the apparent value.*

The polymers $[(CH_3)_2AlOCH_3]_x$ are similar cyclic compounds, forming six- and eight-membered rings[95,96].



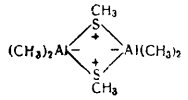
Ferric alkoxides $Fe(OR)_3$ are also trimeric[47,48] and probably have a cyclic structure.

Not only oxygen acts as donor in co-ordination polymers of aluminium, but aluminium halides are known to be dimeric. The cyclic structure of these compounds has been established by electron diffraction[49,50] and X-ray diffraction in the case[51] of Al_2Br_6. $[(CH_3)_2AlBr]_2$ has a similar structure[52].

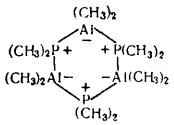


Jaffé[53] applied molecular orbital calculations to the Al_2Cl_6 molecule. The cyclic structure is retained in $Al_2Cl_4H_2$ and $Al_2Br_4H_2$, obtained[54] by the action of LiH on Al_2Cl_6 (or Al_2Br_6).

The compound $(CH_3)_2AlSCH_3$ is a cyclic dimer[55]

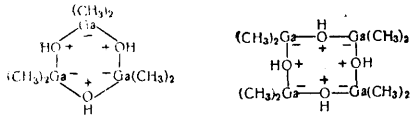


An interesting compound in which phosphorus is the donor is the trimer[55,56] of composition $[(CH_3)_2AlP(CH_3)_2]_3$.

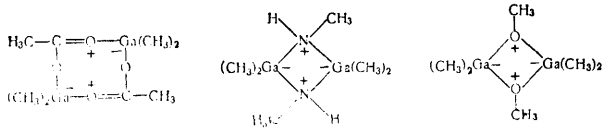


Attempts to obtain similar compounds containing Al and N in the ring were unsuccessful. Thermal decomposition of AlH_3NH_3 yielded[57-59] only acyclic polymers of high molecular weight.

Gallium shows similar co-ordination polymerisation with formation of cyclic compounds. Gallium halides are dimeric: Ga_2Cl_6[60-62] and Ga_2Br_6.[60,61] Kenney and Laubengayer[63] showed that $(CH_3)_2GaOH$ is trimeric in benzene solution. Smith and Hoard[64] used X-rays to study this compound, and demonstrated that it had an eight-membered cyclic structure

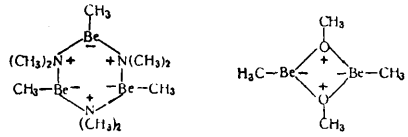


Dimethylgallium acetate $CH_3.COOGa(CH_3)_2$ is a cyclic dimer[65]. The compounds $(CH_3)_2GaNHCH_3$ and $(CH_3)_2GaOCH_3$ are also dimers, and contain four-membered rings[55].

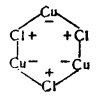


Indium and gallium form analogous compounds. Stone[55] showed that all compounds having the composition $(CH_3)_2M^{III}R$ [where M^{III} = Al, Ga, In, Tl; and R = H_2N–, $(CH_3)_2N$–, $(CH_3)_2P$–, CH_3O–, CH_3S–, CH_3Se–] are polymers having four-, six-, or eight-membered rings. Such polymerisation is the result of the tendency of elements of Group III to form four hybrid sp^3 bonds, one of which can be formed only if a pair of electrons is transferred from a donor (N, O, S, Se, P) (co-ordinate link).

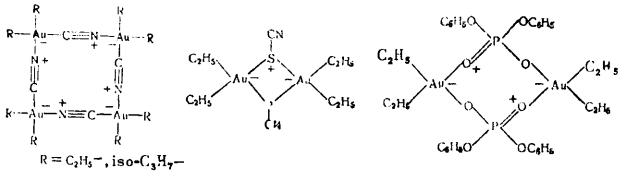
Cyclic compounds are known in which the metal atom possesses sp^2 hybridisation (C.N. = 3). Beryllium forms such compounds[66]: the cyclic trimer $[CH_3BeN(CH_3)_2]_3$, and the dimer $[CH_3BeOCH_3]_2$



Other cyclic co-ordination polymers. Other cyclic co-ordination compounds have been described in the literature. It has been established[67,68] that cuprous chloride in the vapour state contains trimeric Cu_3Cl_3 molecules, which have been shown by electron diffraction[69] to have a cyclic structure. It is probable that the vapours of other metal halides (which are not decomposed at high temperatures) contain cyclic molecules. It is interesting that even the vapours of alkali-metal halides, as Akishin has shown[70,71] contain dimeric and trimeric molecules such as Na_2Cl_2 and Na_3Cl_3.



Among interesting cyclic co-ordination compounds are the dialkylgold cyanide[72,73] $[R_2AuCN]_4$ having a twelve-membered ring, $[(C_2H_5)_2AuSCN]_2$ having a four-membered ring[74], and the compound $[(C_2H_5)_2AuPO_2(OC_6H_5)_2]_2$, which has an eight-membered ring[75]:



R = C_2H_5–, iso-C_3H_7–

Cyclic dimers are known containing halogen bridges between gold atoms, such as Au_2Br_6,[76] and $(R_2AuBr)_2$,[77-79] which are made up of square planar units (Fig. 1*a*). The same structure is shown by the dimeric palladium derivatives $[(CH_3)_3AsPdCl_2]_2$[80] and $[(CH_3)_3AsPdBr_2]_2$[81] as well as by the $Pd_2Cl_4^{2-}$ ions present in an aqueous solution of palladium chloride[82].

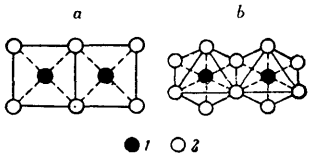
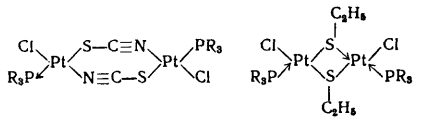


Fig. 1. *a*) Structure of planar cyclic dimer M_2A_6; *b*) structure of dimer $[MA_5]_2$, formed from octahedra.
1) Metal M; 2) ligand A; broken lines - - - co-ordinate links.

Platinum also forms cyclic dimers, for example $[R_3P.PtClSCN]_2$ [83] and $[R_3P.PtSC_2H_5Cl]_2$:[84]



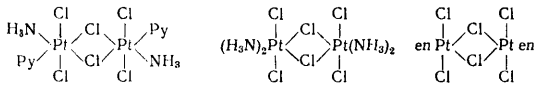
2. CO-ORDINATION POLYMERS WITH CO-ORDINATION NUMBERS 6 AND 8. ALKOXIDES

Most heavy metals form complex compounds having C.N. = 6 and an octahedral structure, and sometimes with C.N. = 8, which corresponds to a cubic structure.

The simplest polymeric compounds containing octahedral structural units are the classical binuclear complexes described in all reviews on the chemistry of complex compounds [11,85-87]. The co-ordination octahedra in these dimers are joined at the corners, edges, or faces.

Several dimeric and trimeric compounds are made up of octahedral structural units. In organic solvents the compounds $NbCl_2(NHCH_3)_2$,[88] $VCl(NHCH_3)_2$,[89] $VCl_2(OR)_2.ROH$, and $MoCl_3(OR)_2$ [90] are dimeric, the metal atom having C.N. = 6 and octahedral co-ordination (Fig. 1*b*). It is interesting that tellurium halides TeX_4 have a trimeric structure[91] in benzene solution, owing to the fact that Te has C.N. = 6.

Platinum derivatives having bridging groups are also known[92-94], their structures being



Recently a large number of compounds having the composition $M(OR)_p$, so-called alkoxides (M = metal, R = aliphatic or aromatic radical, p = valency of metal), have been investigated. In very many cases these compounds are polymeric[44-48,95-121].

It has been found experimentally that the volatility and the degree of polymerisation of alkoxides depend on the atomic radius of the metal and on the degree of branching of the organic radical. The following rules have been established.

(a) The degree of polymerisation is greater the greater the atomic radius of the metal. Thus with a given radical R and metals of the same subgroup, *e.g.* in the series $[M(OR)_4]_x$, where M = Ti, Zr, Hf, Th, the degree of polymerisation in benzene (x) increases together with the atomic radius r_M from Ti to Th (see Table 2).

TABLE 2. Degree of polymerisation of some n-butoxides in solution.

	M in $[M(O.C_4H_9)_4]_x$			
	Ti	Zr	Ce	Th
x	3.0	3.4	4.2	6.3
r_M	1.36	1.48	1.65	1.65

(b) The degree of polymerisation depends on the degree of branching of the alkyl radical R. Compounds in which R is an n-alkyl radical are polymerised to a greater extent than those in which R is a branched radical. Table 3 shows the degree of polymerisation of several alkoxides determined cryoscopically in benzene.

When R is a branched radical, the compounds $M(OR)_p$ are often monomeric.

TABLE 3. Degrees of polymerisation of thorium alkoxides in benzene.[99,100]

R_b in $[Th(OR)_4]_x$	$-CH_3$	$-C_2H_5$	$-n\text{-}C_3H_7$	$-n\text{-}C_4H_9$	$-n\text{-}C_5H_{11}$	$-CH(C_2H_5)_2$	$-CH(CH_3)C_2H_5$	$-CH(CH_3)_2$
x	non-volatile, insol. polymer	non-volatile, insol. polymer	—	6.44	6.20	4.1	4.2	3.8

(c) The degree of polymerisation of alkoxides depends on the nature of the solvent. In inert solvents (benzene, toluene) polymerisation is possible. Solvents containing atoms having donor electrons either diminish (acetonitrile) or prevent (pyridine) polymerisation [103].

(d) The degree of polymerisation of alkoxides decreases with rise in temperature. Ebullioscopic determination of the molecular weight in toluene yields degrees of polymerisation which are lower than in benzene[99,100,102,104]. On the other hand, the energy of intermolecular bonding of alkoxides is low, 10 kcal mole^{-1}.[46]

Bradley[46] explained the structure of alkoxide polymers on the following premises: (*a*) the compound $M(OR)_p$ has that structure in which the co-ordination number of the metal atoms is a maximum; (*b*) the co-ordination number of oxygen does not exceed 4; (*c*) the metal assumes a steric configuration characteristic of a given valency state.

Table 4 gives Bradley's data[46] on the dependence of degree of polymerisation and structure on composition and the co-ordination number of the metal.

The derivatives of ter-, quadri-, and quinque-valent metals have been mainly studied hitherto. Table 5 gives literature references for the known classes of alkoxides.

Table 5 gives also the degree of polymerisation determined cryoscopically in benzene solution. In several cases this is only an apparent value, since the solution contains a mixture of products having different molecular weights. For example, thorium alkoxides $[Th(OR)_4]_x$ have an apparent degree of polymerisation of 6.4, the solution actually containing ~20% of the trimer and 80% of the octamer[99].

Most alkoxides are based on octahedral (C.N. = 6) and cubic (C.N. = 8) units. The octahedra can be combined in twos or threes, forming dimers or trimers (Figs. 1*b* and 2).

TABLE 4. Sterochemistry of alkoxides $[M(OR)_p]_x$.

Compound	C.N. of metal	Stereochemistry of metal (configuration of complex)	Degree of polymerisation (theoretical)	Examples	Refs.
MOR	2	OMO angle 120°	3	unknown	—
	3	pyramidal	3	$[Tl(OR)]_4$	105,106
	4	tetrahedral	3	unknown	—
$M(OR)_2$	4	square planar	4	unknown	—
	6	octahedral	three-dimensional polymer	$[Mn(OR)_2]_x$	107
$M(OR)_3$	4	tetrahedral	2	both in $[Al(OR)_3]_x$	46
	6	octahedral	8		
$M(OR)_4$	6	octahedral	3	$[Ti(OR)_4]_3$, $[Zr(OR)_4]_3$	108, 97
	8	cubic	8	$[Th(OR)_4]_x$ (partly depolymerised)	100
$M(OR)_5$	6	octahedral	2	$[Ta(OR)_5]_2$, $[Nb(OR)_5]_2$	109, 104
$M(OR)_6$	8	cubic	2	$[V(OR)_6]_2$	46

Zirconium, cerium, and thorium can also have a co-ordination number of 8, as in the acetylacetonates, in which the structural unit is cubic. The minimum degree of polymerisation of alkoxides having the composition $[M(OR)_4]_x$ with C.N. = 8 is 8, corresponding to a ring formed by eight cubes (Fig. 3). Thallium alkoxides $[Tl(OR)]_4$ (the benzyloxide [105] and the pentyloxide [106]) have a rather different structure (Fig. 4).

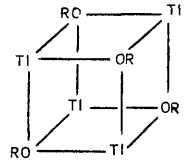


Fig. 4. Structure of tetramer $(TlOR)_4$.

TABLE 5. Composition and degree of polymerisation of metal alkoxides.

Metal	Alkoxide	Degree of polymerisation (found)	Ref.
Tl^{I}	Tl(OR)	4	105, 106
Mn^{II}	$Mn(OR)_2$	insol.	107
Al^{III}	$Al(OR)_3$	2 . . .4	44—49, 110, 117
Fe^{III}	$Fe(OR)_3$	1.5 . . .3.0	47, 48
Ge^{IV}	$Ge(OR)_4$	1	120
Ti^{IV}	$Ti(OR)_4$	1 . . .3.0	97, 111, 114, 115
Sn^{IV}	$Sn(OR)_4$	1	111
Zr^{IV}	$Zr(OR)_4$	1 . . .3.0	97, 111, 121, 116
Th^{IV}	$Th(OR)_4$	1 . . .6.4	99, 100, 110, 111
Ce^{IV}	$Ce(OR)_5$	1 . . .4.3	99—102, 111
Nb^{V}	$Nb(OR)_5$	1 . . .2.0	101, 104
Ta^{V}	$Ta(OR)_5$	1 . . .2.0	98, 101, 103, 104, 109, 112
U^{V}	$U(OR)_5$	3.0	118
U^{VI}	$U(OR)_6$	2.2	46

The structure of alkoxides has not yet been investigated by means of X-ray or electron diffraction: the information quoted above is based only on theoretical considerations and on experimental molecular weights: the study of the structure of alkoxides by direct methods would be of great interest.

Non-volatile and insoluble alkoxides [110], such as $Mg(OCH_3)_2$, $La(OCH_3)_3$, and $Zr(OCH_3)_4$, are also known, these apparently being polymers of high molecular weight.

III. CO-ORDINATION POLYMERS OF HIGH MOLECULAR WEIGHT

In complex compounds the complex-forming metal M has a characteristic co-ordination number n. A given value of n can be achieved in two ways: (a) the central atom M may be surrounded by n "univalent" ligands A, mononuclear complexes with a discrete structure $[MA_n]$ being formed; (b) in compounds of the type $[MA_p]$, in which the apparent co-ordination number p is less than the real value (n), the central atom forms a configuration having C.N. $= n$ by combining with ligands A which form bridges within a polynuclear complex. In the latter case co-ordination polymers $[MA_p]_x$ are produced.

Many "simple" compounds of the type MA_p, in which p is less than the characteristic co-ordination number of the metal, polymerise with the formation of co-ordination compounds of high molecular weight.

1. POLYMERIC COMPLEXES WITH CO-ORDINATION NUMBERS 2 AND 3

The simplest co-ordination polymers of high molecular weight are compounds having the composition MA, in which M is a complex-forming element with C.N. = 2, and A is a

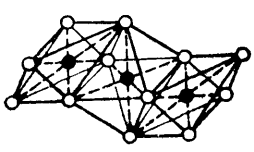


Fig. 2. Structure of octahedral trimer $[MA_4]_3$.

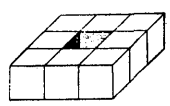


Fig. 3. Structure of octamer $[MA_4]_8$, made up of cubes having faces in common.

bifunctional ligand (capable of forming two links). Polymers of this type have a chain structure:

$$\ldots \rightarrow M-A-\rightarrow M-A\rightarrow M-A\rightarrow \ldots$$

such as that of silver cyanide [122,123], silver thiocyanate [124]

$$\ldots \rightarrow Ag-C\equiv N\rightarrow Ag-C\equiv N\rightarrow Ag-C\equiv N\rightarrow \ldots \quad \ldots \rightarrow Ag-S-C\equiv N\rightarrow Ag-S-C\equiv N\rightarrow \ldots,$$

aurous cyanide [125], and mercuric cyanide [126,127]. Thallium fluoride has a similar linear structure [128].

$$\rightarrow Tl-F \rightarrow Tl-F \rightarrow$$

The complex compound $K[Cu^{I}(CN)_2]$, in which copper apparently has a co-ordination number of 2, is actually polymeric [129] and contains a spiral anion $[Cu(CN)_2^-]_\infty$ (C.N. = = 3 for copper). Only one of the CN groups is involved in forming the chain:

$$\ldots \rightarrow Cu^{I}-CN\rightarrow Cu^{I}-CN\rightarrow Cu^{I}-CN\rightarrow \ldots$$
$$\quad\quad\quad

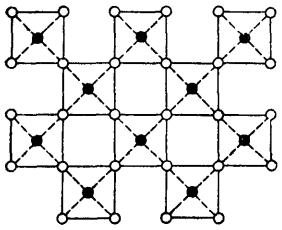


Fig. 8. Structure of planar network $[MA_{4/2}]_\infty N$.

The $[MA_2]_x$ structure is produced by joining square $[MA_4]$ groups at four corners to form a planar two-dimensional network (Fig. 8). Palladium cyanide $Pd(CN)_2$ possesses this type of structure[13].

B. Complexes Having Tetrahedral Units

Both planar and tetrahedral $[MA_4]$ units can be joined at their corners or edges to form one-dimensional chains, two-dimensional networks, or three-dimensional lattices.

(a) Polymers of type $(MA_3]_x$. The joining of tetrahedral units at their corners (as in the silicates) (Fig. 9) was described by Brink and Van Arkel[136] in the compounds $(NH_4)_2[Cu^ICl_3]$ and $(NH_4)_2[Cu^IBr_3]$, which consist of infinite-chain anions of the structure $[Cu^IX_3^{2-}]_\infty$ made up of tetrahedral $[CuX_4]$ units. The same structure was also found in $K_2[CuCl_3]$, $Cs_2[AgCl_3]$, $Cs_2[AgI_3]$,[137] $K_2[AgI_3]$, $Rb_2[AgI_3]$, and $(NH_4)_2[AgI_3]$.[138] Such polymeric chains, having the composition $[MA_{2+2/2}]_\infty K$, can also be expected in compounds of zinc, beryllium, etc. The fluoroberyllates $M^I[BeF_3]$[139-141] apparently have a structure of this type, especially as $NaBeF_3$ is isomorphous with β-$CaSiO_3$.[142]

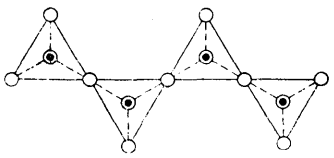


Fig. 9. Structure of chain of tetrahedra $[MA_{2+2/2}]_\infty K$ with common corners.

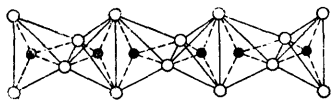
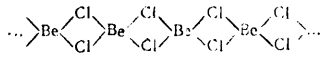


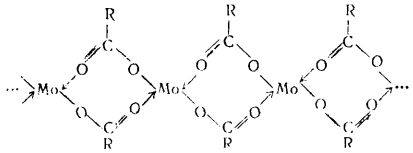
Fig. 10. Structure of chain of tetrahedra $[MA_{4/2}]_\infty K$ with edges in common.

(b) Polymers of type $[MA_2]_x$. If tetrahedra are joined at their edges, the structure $[MA_{4/2}]_\infty K$ results. Thus infinite chains of this type (Fig. 10) are formed in the structure of beryllium chloride $BeCl_2$:[143]

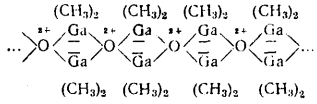


Double chains of tetrahedra are also known, in the structures of $Cs[Cu_2Cl_3]$ and $Cs[Ag_2I_3]$.[144]

The same structure (Fig. 10) has been ascribed to salts of bivalent molybdenum with organic acids[145]:



An interesting polymer, in which oxygen is situated at the centre of the tetrahedron, with metal atoms at the corners, is the compound $[(CH_3)_2Ga]_2O$, which has been assigned the structure[146]



Tetrahedral units combine less often to form two-dimensional networks (Fig. 11) $[MA_{4/2}]_\infty N$ (N = *Netzstruktur*[131] = network structure), as occurs in red mercuric iodide[147] and in γ-$ZnCl_2$.[148]



Fig. 11. Structure of red mercuric iodide HgI_2 (two-dimensional layer).

Tetrahedral $[MA_4]$ units can sometimes unite at four corners to form three-dimensional lattices having the structure $[MA_{4/2}]_\infty G$ (G = *Gitterstruktur*[131] = lattice structure). Thus, for example tetrahedral BeF_4^{2-} groups sometimes form three-dimensional lattices. Warren and Hill[149] showed that vitreous BeF_2 has a similar structure to vitreous silica. Brandenberger[150] and Wyckoff[151] prepared from $(NH_4)_2BeF_4$ beryllium fluoride having a β-cristobalite structure. Novoselova and her coworkers[152] also obtained a new form of beryllium fluoride with the β-cristobalite structure. Beryllium fluoride is a structural analogue of silicon dioxide[153,154]. The Be–F bond is not purely ionic but has some covalent character[139], making possible the formation of fluoroberyllates, which are similar to silicates in structure.

Recently Brehler[155] has shown that α-$ZnCl_2$ and β-$ZnCl_2$ possess a three-dimensional tetrahedral lattice in which the $ZnCl_4$ groups are joined at their corners. Beryllium hydroxide β-$Be(OH)_2$[156] and zinc hydroxide[157] have a structure in which a metal atom is surrounded tetrahedrally by four OH groups. Zinc cyanide[158] and cadmium cyanide[159] have three-dimensional polymeric structures of the anticuprite type (co-ordination number of metal = 4).

(c) Polymers of type $[MA]_x$. A three-dimensional lattice consisting of tetrahedral units, $[MA_{4/4}]_\infty G$, is formed by the two modifications of zinc sulphide — wurtzite[160] and zinc blende[161,162]. This type of structure is found in very many compounds[11,13,160-168]:

Sulphides:	ZnS, CdS, BeS, HgS, MnS
Oxides:	ZnO, BeO, CuO
Selenides:	ZnSe, CdSe, HgSe
Tellurides:	ZnTe, CdTe, HgTe
Antimonides:	InSb, GaSb, AlSb
Arsenides:	GaAs, AlAs, BAs
Phosphides:	GaP, AlP, BP
Iodides:	CuI, AgI
Bromides and chlorides:	CuBr, CuCl.

In other compounds — PbO, SnO, PdO, PtO,[169] and $Ag^{II}O$[170] — the metal has the same co-ordination number of 4, but the structure is different.

Co-ordination polymers in which the metals have a co-ordination number of 4 are very common. Table 6 gives possible co-ordination polymers made up of structural units having a co-ordination number of 4.

TABLE 6. Possible structures of co-ordination polymers of co-ordination number of 4.

Apparent C.N.	Composition of polymers	Stereochemical formula	Modes of formation of polymer: joining of square planar units	Modes of formation of polymer: joining of tetrahedral units
3	MA_3	$[MA_{2+2/2}]_\infty K$	two corners in common: *cis* $[CuCl_3]Cs$ (Fig. 5); *trans* (Fig. 6)	two corners in common: $K_2[CuCl_3]$ (Fig. 9)
2	MA_2	$[MA_{4/2}]_\infty K$	two edges in common: $PdCl_2$ (Fig. 7)	two edges in common: $BeCl_2$ (Fig. 10)
		$[MA_{4/2}]_\infty N$	four corners in common: $Pd(CN)_2$ (Fig. 8)	four corners in common: HgI_2 (two-dimensional network) (Fig. 11)
		$[MA_{4/2}]_\infty G$		four corners in common: BeF_2 (three-dimensional lattice)
1	MA	$[MA_{4/4}]_\infty G$		four corners in common: ZnS (three-dimensional lattice)

3. POLYMERIC COMPLEXES WITH CO-ORDINATION NUMBER 6

The number of complex compounds in which the central atom has a co-ordination number of 6 is very large. This value is characteristic of Cd^{II}, Cr^{III}, Co^{III}, Al^{III}, Fe^{III}, Ir^{III}, Rh^{III}, Sc^{III}, Sn^{IV}, Pb^{IV}, Pt^{IV}, Ru^{IV}, Ti^{IV}, Sb^{V}, etc.[85-87] Complex ions $[MA_6]$ of these elements have an octahedral configuration: the metal atom M is surrounded by six ligands situated at the corners of an octahedron.

A co-ordination number of 6 is achieved in polymeric compounds in which the structural units are joined at the corners, edges, or faces. This is possible when A is a bi- or ter-functional ligand able to form two or three bonds.

(a) Polymers of type $[MA_5]_x$. If the octahedral $[MA_6]$ units are joined by having a corner in common, forming an infinite chain (Fig. 12), the resulting polymers $[MA_5]_x$ have the stereochemical formula $[MA_{4+2/2}]_\infty K$.

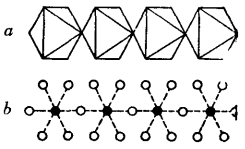
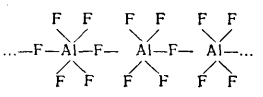


Fig. 12. Structure of chain of octahedra $[MA_{4+2/2}]_\infty K$ having common corners: *a*) stereochemical view; *b*) co-ordinate links (chemical structure).

Aluminium is known to have a co-ordination number of 6 with respect to fluorine, *e.g.* in cryolite $Na_3[AlF_6]$. In the insoluble compound $Tl_2[AlF_5]$ the co-ordination number of the aluminium is not 5, as might appear, for this compound contains a polymeric anion $[AlF_5^-]_\infty$, which has a linear structure[171].

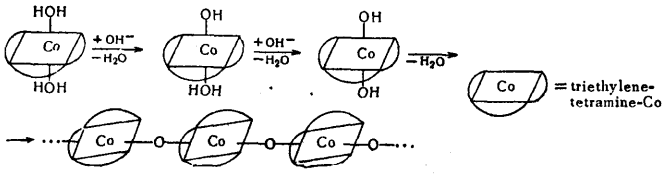


The thallium ions are distributed around the macromolecular chain.

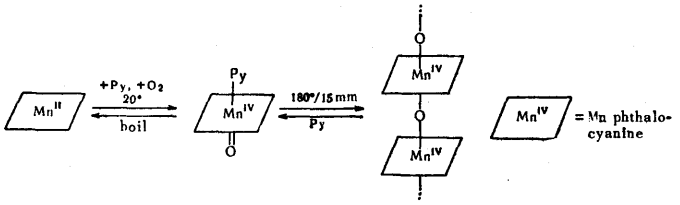
The compound SbF_5 contains linear molecules[172] made up of octahedral units, $-SbF_4-F-SbF_4-F-$. The complex polymers $[IrPy_2Cl_3]_x$ and $[RhPy_2Cl_3]_x$ (Py = pyridine), obtained by Delépine[173], probably have a similar structure.

When a solution of the triethylenetetramine complex of tervalent cobalt is made alkaline, a linear polymer[174] $[CotnO]_x$ (tn - triethylenetetramine) is formed in which the

octahedral complexes have oxygen atoms in common (in the axial positions):

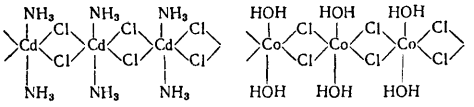


A similar polymer is obtained also from manganese phthalocyanine[175]:



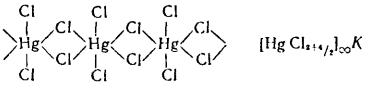
(b) Polymers of type $[MA_4]_x$. If the octahedra are joined edge to edge in the chain, complex polymers having the stereochemical formula $[MA_{2+4/2}]_\infty K$ are formed. This mode of union can be effected in two ways, with the formation of straight (Fig. 13) or kinked (Fig. 14) chains.

In the complex compound $[CdCl_2(NH_3)_2]$ the central cadmium atom has a co-ordination number of 6, since the complex is made up of octahedral units (Fig. 13). The chlorine atoms form bridging groups between the cadmium atoms, and the ammonia molecules occupy the free co-ordination positions. This structure corresponds to the formula $[Cd(NH_3)_2Cl_{4/2}]_\infty K$, and was established by means of X-rays[176]; another example is $CoCl_2.2H_2O$:[177]

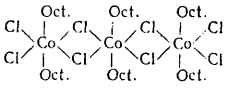


Of course, not all $[M(NH_3)_2Cl_2]$ complexes have a polymeric structure of this type: $[Zn(NH_3)_2Cl_2]$ is a mononuclear tetrahedral complex[178], and the compound $[Pt(NH_3)_2Cl_2]$ has a square planar structure (co-ordination number of 4 for zinc and platinum).

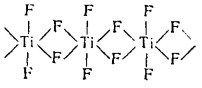
This structure is found in the compounds $K_2[SnCl_4].2H_2O$[179] and $K_2[HgCl_4].H_2O$,[180] in which chlorine atoms form bridging groups and the K^+ ions and water molecules surround the polymeric chain.



Complex polymers of this type have also been detected in solution. In octanol[181], for example, nickel and cobalt chlorides form polymers of the following type:



The fluorides TiF_4 and SnF_4 are assigned a linear polymeric structure[11]



Hoppe[182] considers that SnF_4 has a two-dimensional layer structure (see below). The mode of combination of octahedra shown in Fig. 14 has not been observed in any complex compound. Brookite TiO_2 contains chains of octahedra of this type, but the chains are linked by common oxygen atoms to form a three-dimensional lattice.

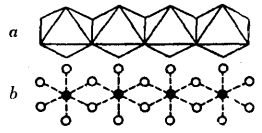


Fig. 13. Structure of chain of octahedra $[MA_{2+4/2}]_\infty K$ having common edges (linear chain). For key see Fig. 12.

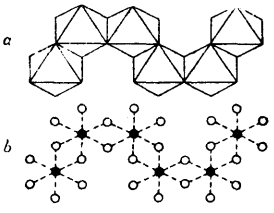


Fig. 14. Structure of chain of octahedra $[MA_{2+4/2}]_\infty K$ having common edges (wavy chain). For key see Fig. 12.

Another possibility in $[MA_4]_x$ compounds is the linking of the octahedral groups at four corners to form a planar two-dimensional network (layer structure) (Fig. 15). This structure has been observed in the following compounds: $K_2[NiF_4]$,[183] $K_2[CuF_4]$,[184] $Tl[AlF_4]$,[185] $K[AlF_4]$,[186] SnF_4,[182] $K_2[MgF_4]$,[187] $La_2[NiO_4]$,[188] $Ba_2[SnO_4]$ and $Ba_2[PbO_4]$,[189] and others[190–193]. It was established that β-$UO_2(OH)_2$ has a structure of the same type[194], the OH groups in the plane forming "equatorial bonds", and the oxygen atoms "uranyl bonds".[195]

(c) Polymers of type $[MA_3]_x$. In many compounds having the composition MA_3 the actual co-ordination number of the central atom is 6. The simplest way in which this composition can be achieved is for the octahedra to be joined along three edges (Fig. 16) to form a planar two-dimensional network of the type $[MA_{6/2}]_\infty N$. This structure is shown by several anhydrous halides of ter-

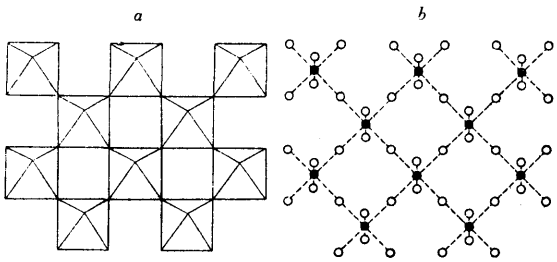


Fig. 15. Structure of octahedral layer $[MA_{2+4/2}]_\infty K$ (octahedra with common corners). For key see Fig. 12.

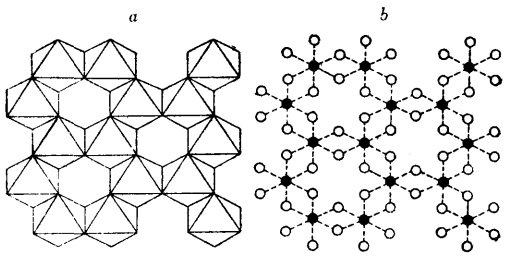


Fig. 16. Structure of octahedral layer $[MA_{6/2}]_\infty N$ (octahedra with common edges). For key see Fig. 12.

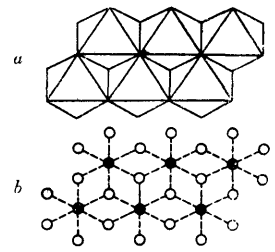


Fig. 17. Structure of double octahedral chain $[MA_{1+2/2+3/3}]_\infty K$ (NH_4CdCl_3 structure). For key see Fig. 12.

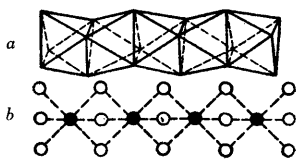


Fig. 18. Structure of octahedral chain $[MA_{6/2}]_\infty K$ (octahedra with faces in common). For key see Fig. 12.

valent metals: $CrCl_3$,[196] $RuCl_3$,[197] $AlCl_3$,[198] $FeCl_3$,[199] AlF_3,[200-201] BiI_3,[13] etc.; also by hydroxides of tervalent metals such as $Al(OH)_3$ (hydrargillite)[202], and some complex compounds having macromolecular anions, such as $NH_4[HgCl_3]$.[203]

In the lattice of these compounds the metal atom is surrounded by six halogen atoms (or OH groups), which form bridging groups with other nuclei. Every halogen atom is combined with two metal atoms.

Another way in which octahedra can be combined to form a polymer of type $[MA_3]_x$ is shown in Fig. 17, corresponding to the stereochemical formula $[MA_{1+2/2+3/3}]_\infty K$. This type of structure is found in $NH_4[CdCl_3]$.[204,205]

Combination of octahedra at their opposite faces yields a chain having the composition $[MA_3]_x$ and of type $[MA_{6/2}]_\infty K$ (Fig. 18). This occurs, for example, in $Cs[NiCl_3]$,[206] which contains the $[NiCl_3]_x^{x-}$ chain.

When the octahedral structural units are joined at six corners, a three-dimensional lattice of the rhenium trioxide ReO_3 type[207], having the formula $[MA_{6/2}]_\infty G$, is formed (Fig. 19). The ReO_3 structure is found also in the compounds WO_3, MoO_3, and CrO_3, which are not co-ordination but ordinary polymers, since the co-ordination number is then equal to the valency of the metal.

The ferricyanides of iron are based on the rhenium trioxide type of structure. X-Ray diffraction has established that ferric and ferrous ferricyanides[208], like other ferrocyanides of the transition metals[209-213], have similar structures. In $Fe^{III}[Fe^{III}(CN)_6]$ the iron atoms form a cubic lattice, the CN groups being situated on the edges of the cube and being combined with the iron by the nitrogen atom (N → Fe co-ordinate links) and by the carbon atoms. This results in the three-dimensional lattice $[Fe(CN)_{6/2}]_\infty G$ (Fig. 19). Since not all the Fe atoms are tervalent in ferrous ferricyanides, the lattice is negatively charged, and is neutralised by alkali-metal ions situated interstitially in the lattice, as represented by the formula $K[Fe^{II}Fe^{III}(CN)_6]$. In copper ferrocyanide some of the iron atoms have been replaced by copper atoms, the correct formula of this compound being $K_2[CuFe^{II}(CN)_6]$. It is noteworthy that the

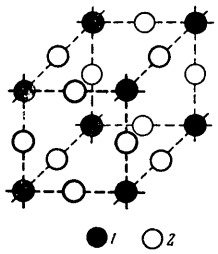


Fig. 19. Rhenium trioxide type of structure $[MA_{6/2}]_\infty G$: 1) Fe, Re, or other metal (C.N. = = 6); 2) CN, O, or other ligand.

ferrocyanides and ferricyanides of the alkali and alkaline-earth metals are not polymeric, their lattice containing separate $[Fe(CN)_6]^{4-}$ or $[Fe(CN)_6]^{3-}$ ions and metal ions. Macromolecular structures are formed only when transition metals such as copper, iron, etc., themselves capable of forming complexes with CN groups, are present in the outer sphere of the complex ions. Such compounds may be termed "supercomplexes". It may be supposed that, when the outer-sphere cation can itself form co-ordinate links with ligands, and a multifunctional (multidentate) ligand is present, the ligands form bridging groups between the metal atoms in the lattice, resulting in a co-ordinated macromolecular structure. Hence most salts formed by complex $[MA_n]^{p-}$ anions (where A is a bi- or tri-dentate ligand) with transition metals are co-ordination high polymers. X-Ray investigation of such compounds is of great interest from the point of view of polymer chemistry.

Another polymer having the rhenium trioxide structure is the compound InF(OH).[214]

The structure of perovskite $CaTiO_3$ is related to the ReO_3 structure[168,215,216]. The anion of the original acid is polymeric, forming a $(TiO_3)_x^{2x-}$ lattice with a rhenium trioxide type of structure; the Ca cations are arranged interstitially in the cubic lattice. This structure exists in a large number of compounds:

1) in double oxides[217-221]:

$CaTiO_3$	$NaNbO_3$	$NaTaO_3$	$LaGaO_3$	KIO_3	$SrSnO_3$	$CaZrO_3$
$SrTiO_3$	$KNbO_3$	$KTaO_2$	$LaAlO_3$	$RbIO_3$	$CaSnO_3$	$BaZrO_3$
$BaTiO_3$			$LaFeO_3$			

2) in complex compounds:

$K[MnF_3]$[218], $K[NiF_3]$[192], $Cs[HgCl_3]$[222], $Cs[CdCl_3]$[224], $CsAgCl_3 \cdot CsAuCl_3$[226], $Rb[MnF_3]$[218], $K[MgF_3]$[222], $Cs[HgBr_3]$[225], $Cs[CdBr_3]$[224], $Cs[AuCl_3]$[226].

An interesting $[MA_3]_x$ polymer is represented by the compound $[SAg_3]NO_3$, in which sulphur acts as the central atom[227], surrounded by six silver atoms. The $[SAg_6]$ groups are joined to form a macromolecular $[SAg_3]_x$ lattice.

(d) Polymers of type $[MA_2]_x$. It may be imagined from the above that a co-ordination number of 6 can also be achieved in the structures of some compounds having an apparent co-ordination number of 2, the co-ordinate octahedra being joined at six edges to form a two-dimensional layer lattice $[AB_{6/3}]_\infty N$ (Fig. 20). The structure of lead iodide has been investigated quite thoroughly[228-232]. Each lead atom is surrounded by six iodine atoms, and every iodine atom forms co-ordinate links with three lead atoms†. Layer structures are also encountered in other *halides*, such as CdI_2,[232-244] $CdBr_2$,[229-232,245] CdIBr,[246] CaI_2,[247] $MgBr_2$,[248] $MnCl_2$, $MnBr_2$,[248] MnI_2,[249] FeI_2,[249] $FeBr_2$,[248] $FeCl_2$,[250] CoI_2,[249] $CoCl_2$,[251] $NiCl_2$,[252] NiI_2,[252] VCl_2,[253,254] $HgBr_2$,[255] and yellow HgI_2;[255] in *sulphides*, *selenides*, and *tellurides* $TiSe_2$, $TiTe_2$, SrS_2, $ZrSe_2$,[256] and Tl_2S;[257] *hydroxides* $Cd(OH)_2$,[249,258] $Mg(OH)_2$,[259] α-$Zn(OH)_2$,[260,261] β-$Zn(OH)_2$,[262] $Ni(OH)_2$,[263] and $Co(OH)_2$;[264] *mixed hydroxides*, Ni–Zn and Co–Zn;[265] and in *basic salts*,[266-271] for example Zn(OH)Cl[272] and Cd(OH)Cl.[274]

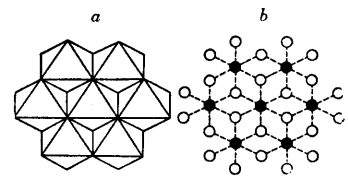


Fig. 20. Structure of octahedral layer $[MA_{6/3}]_\infty N$. For key see Fig. 12.

Krebs showed[273] that covalent character is superimposed on the ionic state of the bond in typical salts and in layer structures, confirming the polymeric structure of these compounds.

Other types of structure having the co-ordination number of 6 are found in AlO.OH,[275,276] AlOCl,[277] ReO_2,[278] $HCrO_2$,[279] etc. The rutile TiO_2 structure is based on straight chains of octahedra (Fig. 13) linked to form a three-dimensional lattice[11], while the structure of brookite, TiO_2, is based on wavy chains of octahedra (Fig. 14) linked three-dimensionally.

These ways of forming macromolecular structures based on octahedral units are set out in Table 7.

4. OTHER POLYMERS

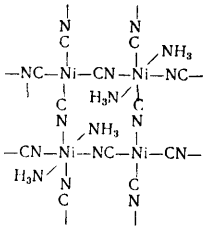
The examples quoted here do not, of course, exhaust all the possible ways in which co-ordinated macromolecular structures may be formed. Co-ordinated polymeric structures may be produced by combining different structural units.

† Iodine can also act as the central atom with C.N. = 3, for example in the complex compound $[IAg_3](NO_3)_2$.[233]

TABLE 7. Possible structures of co-ordination polymers C. N. = 6.

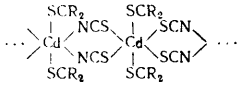
Apparent C.N.	Composition of polymer	Stereochemical formula	Mode of combination of octahedra
5	MA_5	$[MA_{4+2/2}]_\infty K$	chain of octahedra with two corners in common (Fig. 12)
4	MA_4	$[MA_{2+4/2}]_\infty K$	chain of octahedra with two edges in common (Figs. 13 and 14)
		$[MA_{2+4/2}]_\infty N$	two-dimensional layer of octahedra with four corners in common (Fig. 15)
		$[MA_{1+2/2+3/3}]_\infty K$	double chain of octahedra with four edges in common (Fig. 17)
3	MA_3	$[MA_{6/2}]_\infty K$	chain of octahedra with faces in common (Fig. 18)
		$[MA_{6/2}]_\infty N$	two-dimensional layer of octahedra with three edges in common (Fig. 16)
		$[MA_{6/2}]_\infty G$	three-dimensional lattice of octahedra with six corners in common (Fig. 19)
2	MA_2	$[MA_{6/3}]_\infty N$	two-dimensional layer of octahedra with six edges in common (Fig. 20)

The compound KCr_3O_8, for example, contains[280] CrO_4 tetrahedra and CrO_6 octahedra. In the compounds $Ni(CN)_2 . NH_3$[281] half the nickel atoms have a co-ordination number of 6, and the other half a co-ordination number of 4.

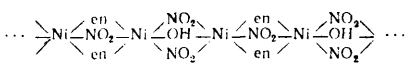


In the compound V_3O_5 the VO_6 octahedra are joined in a complicated manner — at the corners, edges, and faces simultaneously[282]. Many examples of such structures can be found in the literature on structural chemistry.

An interesting co-ordination polymer is di-(2-thioimidazolidine)cadmium thiocyanate, described by Cavalca *et al.*[283] It is made up of octahedra linked by SCN groups to form an infinite chain



The compound $Ni_2en_2(NO_2)_3OH$ has the structure[284]

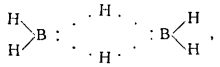


Thus many compounds which we have been accustomed to regard as "simple" are actually polymeric. The somewhat paradoxical conclusion can be drawn that binary compounds (having a polymeric co-ordinate structure), which are regarded as "simple compounds", have more complicated structures than the "complex" compounds (which have a discrete, non-polymeric structure). Hence it follows that the concept of "complex compound" is quite arbitrary: the chemistry of complex compounds must include also those binary compounds whose structures bring them into the class of co-ordination polymers. We must, of course, distinguish the polymeric $CuCl_2$ from the mononuclear hydrate $CuCl_2.2H_2O$, which has a discrete structure. Among the compounds $[CdCl_2(NH_3)_2]$, $[ZnCl_2(NH_3)_2]$, and $[PtCl_2.(NH_3)_2]$, only the first is polymeric. It is therefore necessary, in the chemistry of complex compounds, to use a classification based on the structure of the complexes and not solely on the empirical formula.

IV. ELECTRON-DEFICIENT POLYMERS

We have already mentioned the tendency of elements to form as many bonds as possible by drawing unpaired electrons into vacant orbitals, with formation of a larger number of bonds than would correspond to the classical valency. Sometimes the tendency of elements to increase the number of bonds by utilising unoccupied valency orbitals is so strong that polymerisation takes place even in compounds in which the electrons are sufficient only to form the bonds corresponding to the valency of the element. In the compounds BH_3, $Be(CH_3)_2$, $Al(CH_3)_3$, $Pt(CH_3)_4$ all the electrons are involved in normal covalent bonds, which elementary classical valency theory describes as two-centre electron-pair bonds. Nevertheless, these compounds do form polymers because of the tendency of B, Be, Al, and Pt atoms to make full use of their valency orbitals. The resulting polymers contain a larger number of chemical bonds than of electron pairs necessary for this purpose. Such compounds are therefore said to be "electron-deficient". The polymerisation of these compounds is made possible by the formation of three-centre and many-centre bonds, *i.e.* bonds in which the electron pair is situated in the field of three or more nuclei[16,285,286].

The simplest polymer of this type is diborane B_2H_6. It has been established that this compound has a structure in which two hydrogen atoms act as bridging groups between the two boron atoms[287-291]



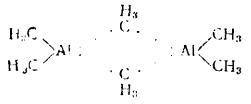
forming a B_2H_2 ring, while the other four hydrogen atoms remain outside this ring. Several hypotheses have been put forward to explain the nature of the B...H...B bonds[292].

The diborane molecule contains eight atoms, so that it should have seven covalent bonds, *i.e.* fourteen electrons, whereas it actually has only twelve electrons, eight of which are used in the four outer B–H bonds. Only four electrons remain for the B...H...B bonds. The mechanism whereby four electrons can link four atoms has been clarified by the theory of molecular orbitals. It was found that the hybrid-orbitals of the two boron atoms can overlap the 1*s* orbital of the hydrogen atom and the formation of the B_2H_2 ring is based on that of two three-centre B...H...B bonds.

The idea of many-centre orbitals was extended to explain the structure of other boron hydrides:[293] B_5H_9,[294,295] B_5H_{11},[296] B_4H_{10},[297,298] B_6H_{10},[299] $B_{10}H_{14}$,[300] etc.[301-305], and was used to interpret the structures of other electron-deficient molecules.

An interesting polymeric boron compound having many-centre bonds is B_4Cl_4, obtained by Urry *et al.*[306] This compound might have been homocyclic, but electron diffraction[307,308] showed that the boron atoms were arranged at the corners of a regular tetrahedron and were held together by many-centre bonds involving the $3p\pi$ electrons of the chlorine.

Trimethylaluminium is a dimer[309]. Its structure was determined by means of electron diffraction[310,311] and involves methyl bridges



The Al...CH_3...Al bonds are three-centred, and are produced by the overlapping of the vacant orbitals of the aluminium atoms and the *p* orbitals of the CH_3 group. In $(CH_3)_2AlCl$ and CH_3AlCl_2, which also are dimeric, chlorine atoms act as bridging groups:



These molecules are not electron-deficient, but it is probable that the Al...Cl...Al bonds are also three-centred.

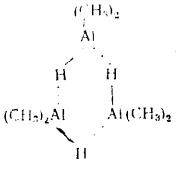
It is interesting that $Ga_2(CH_3)_6$ is less stable, probably because the large size of the gallium atom prevents sufficient overlapping of the three orbitals.

Formation of many-centre bonds may explain the structure of aluminium hydride $(AlH_3)_x$, in which every aluminium atom is surrounded by six hydrogen atoms[312].



The polymeric nature of gallium hydride $(GaH_3)_x$[313-315] and indium hydride $(InH_3)_y$[316] can also be explained in this way.

Dimethylaluminium hydride $HAl(CH_3)_2$ is a cyclic trimer[317,318]. Other similar compounds, for example $[HAl.(C_2H_5)_2]_3$ and $[HAl(iso\text{-}C_4H_9)_2]_3$, are also electron-deficient polymers containing many-centre bonds



Indium has a higher co-ordination number than aluminium, and therefore trimethylindium is a tetramer $[In(CH_3)_3]_4$. This compound has a cubic structure[319], a proportion of the methyl groups, situated at the corners of the cube, serving as bridges. The tetrameric molecule is formed by means of many-centre orbitals. The external In–CH_3 bonds are ordinary covalent bonds.

X-Ray analysis has shown that tetramethylplatinum $[Pt(CH_3)_4]_4$ has a similar composition[320] and structure[321] (Fig. 21). The compound $[(CH_3)_3PtCl]_4$ has an analogous structure, the chlorine and platinum atoms being arranged at the corners of a cube[321]. In these compounds the platinum has a co-ordination number of 6 owing to the utilisation of d^2sp^3 orbitals, the tendency to complete utilisation of which[16] leads to polymerisation. Tetramethyl-lead $Pb(CH_3)_4$ is not polymeric, since lead has only four sp^3 orbitals.

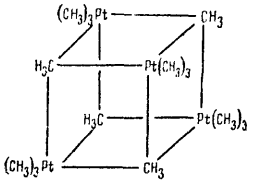


Fig. 21. Structure of $[Pt(CH_3)_4]_4$.

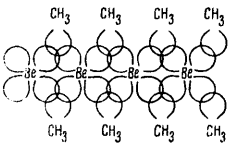
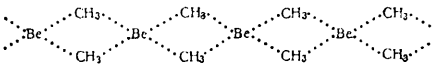


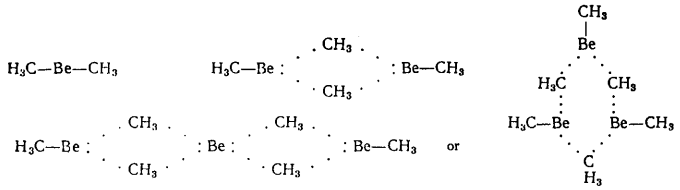
Fig. 22. Formation of three-centre bonds in $[Be(CH_3)_2]_x$ chain.

Many-electron many-centre bonds can also govern the formation of electron-deficient polymers of high molecular weight. X-Ray diffraction patterns have shown[311] that $Be(CH_3)_2$ consists of endless linear chains, the beryllium atoms being linked by methyl bridges (Fig. 22).



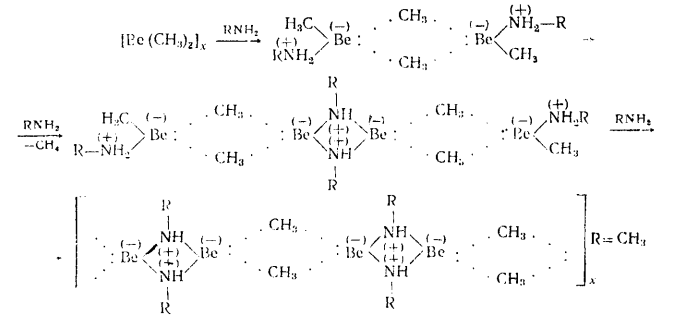
The beryllium atoms are surrounded tetrahedrally by four CH_3 bonds. The Be...CH_3...Be bonds are weaker than simple covalent bonds, and can be regarded as "half-bonds"; this depends also on the bond length[322] Be...CH_3 = 1.92 Å (normal covalent Be–C bonds have a length of 1.73 Å).

Monomeric, dimeric, and trimeric molecules are formed in $Be(CH_3)_2$ vapour



Electron-deficient compounds behave chemically as Lewis-acids: *i.e.* they react with electron-donors. This is because a two-centre electron-pair bond is more stable than a pair of unshared electrons and than a three-centre electron-pair bond[285]. It is therefore clear why boron hydrides react readily with amines and other electron-donors[305,324,325].

The interesting reactions of $[Be(CH_3)_2]_x$ with amines[326], ethers, and phosphines[327] can be explained in a similar manner. On reaction with primary amines the polymer is broken down with the formation of $Be-\overset{R}{\underset{}{N}}H-Be$ co-ordinate bridges and a polymer containing both two-centre co-ordinate links and three-centre bonds:



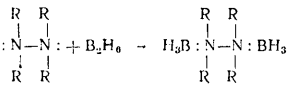
In this way groups of compounds are obtained having the general composition

$$[(CH_3)_2Be]_x[(CH_3)_3P]_y \quad x = 1\ldots5;\ y = 1\ldots3^{327}$$

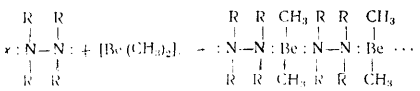
$$[(CH_3)_2Be]_x[(CH_3)_2O]_y \quad x = 1, 2, 6;\ y = 1\ldots3^{327}$$

$$[(CH_3)_2Be]_x[(CH_3)_3N]_y{}^{326}$$

Recently an interesting derivative of tetramethylhydrazine and diborane has been prepared[328]

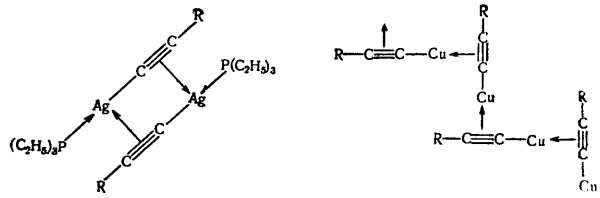


Dimethylberyllium, which has two vacant orbitals, is able to form a linear polymer of high molecular weight

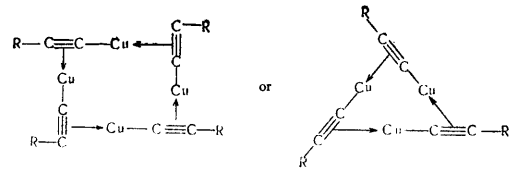


Although electron-deficient compounds are unstable, which would hinder their practical application, they may be of interest for the synthesis of other chain polymers.

The recently prepared acetylenic polymers of univalent copper and silver[329] can probably be included in the same group: $(C_2H_5)_3PAgC{:}CR$ is dimeric in nitrobenzene, while the corresponding copper compound is trimeric or tetrameric. The following structures are assumed for these compounds



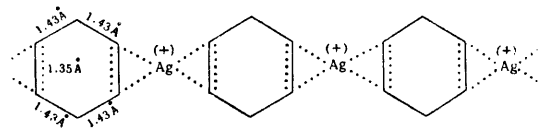
The present reviewer suggests a cyclic structure for the copper compound



The bond between the metal atom and the C:C group is probably three-centred. The same type of bond is probably present also in the compound $C_6H_6.AgClO_4$, which can be represented as a polymeric chain[330]

$$\cdots C_6H_6\cdots Ag\cdots C_6H_6\cdots Ag\cdots$$

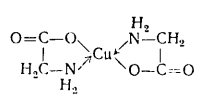
in which the benzene rings are strongly distorted (four C–C bonds of 1.43 Å, and two C–C bonds of 1.35 Å).



Such polymers very probably exist. The study of electron-deficient compounds is only in its initial stages, and the results of investigations in this field are of great scientific value.

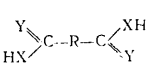
V. POLYMERIC CHELATE COMPOUNDS

Chelate compounds[85-87,331] are of great importance in the chemistry of complex compounds; they are complexes in which the metal atom forms part of a ring (usually five- or six-membered), for example



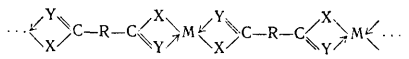
Berlin and Matveeva[332] have recently suggested the term "chelatophor" for groups which are able to form chelate rings.

Organic compounds of the type



(X = O, S, NH, etc.; Y = O, S, NH) can react with metal

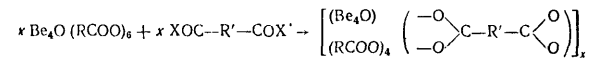
ions to form chelate polymers having the general structure



Since the chemistry of chelate polymers has been discussed in detail by Berlin and Matveeva[332], we shall consider only examples of compounds in which metal atoms alternate with organic groups to form the main chain. Several classes of compounds of this type are known.

Elliot[333] obtained polymers of cobalt with bis-α-amino acids. It would be useful to study thioamine acids, amides, and other acid derivatives of similar structure with a view to obtaining new chelate polymers.

Sometimes merely the presence of a carboxyl group at the ends of a hydrocarbon chain is sufficient for the formation of co-ordination polymers. Thus basic beryllium acetate $(CH_3.COO)_6Be_4O$ forms polymers with dibasic organic acids

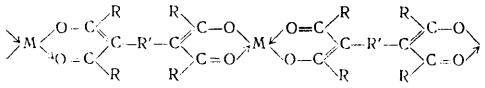


where X = OH, OR.

Polymers containing beryllium can be prepared from succinic[334,335], adipic, sebacic, isophthalic, and terephthalic acids[336].

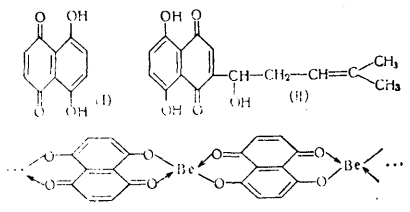
Even copper salts of α,ω-dicarboxylic acids have a two-dimensional macromolecular structure[337]. Compounds of univalent copper with α,ω-dinitriles $[Cu(NC.R.CN)_2]NO_3$ are also polymeric, as is shown by an X-ray investigation of the complexes of succinonitrile[338], glutaronitrile[339], and adiponitrile[340].

A large number of co-ordination polymers have been obtained by the reaction of tetraketones with Be, Cu, Ni, Zn, Co, Fe, Pd, Mn, Sr, Cd, etc.[341-344]

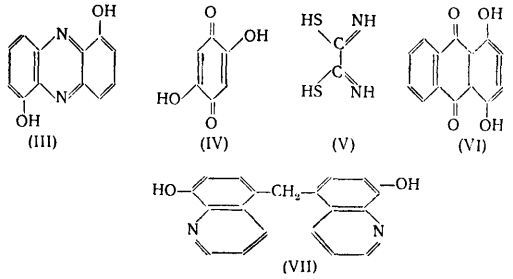


Chelate polymers of aluminium have a similar structure[345].

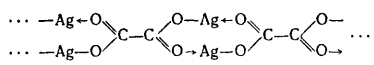
Hydroxynaphthaquinones are also able to form polymers. Linear polymers of beryllium with naphthazarin and alkannin have been obtained[346]



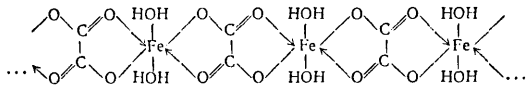
Polymers are known containing various metal ions and 1.6-dihydroxyphenazine (III),[347] 2,5-dihydroxybenzoquinone (IV),[347] rubeanic acid (V),[348,349] 5-formylsalicylaldehyde,[350] quinizarin (VI),[351] bis-8-hydroxyquinolinylmethane (VII),[352] and other ligands[353-359]



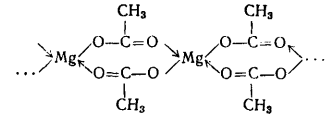
Among interesting polymers are those in which the chelate ring contains two metal atoms, *e.g.* silver oxalate[330]:



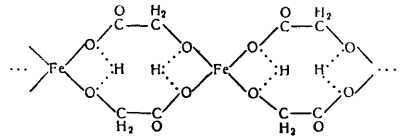
Ferrous oxalate also is a linear polymer[361]:



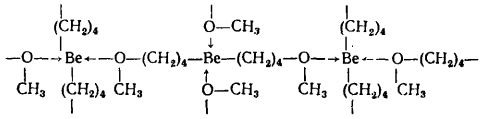
The high viscosity of concentrated solutions of magnesium acetate is explained by the formation of polymers[362,363]



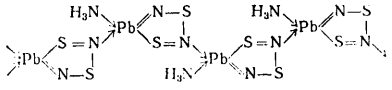
Infra-red spectra have shown that ferrous glycollates are polymers of similar type[364]



Interesting polymers are encountered among organic derivatives of beryllium[365]

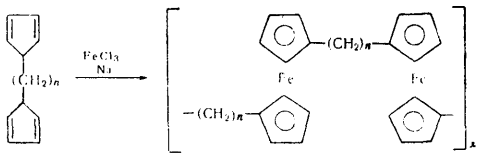


The existence of purely inorganic chelate polymers is possible, for example $Pb(NS)_2NH_3$:[366]

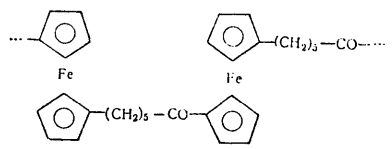


Progress in metallocene chemistry has made it possible to obtain new types of polymers containing such groups in

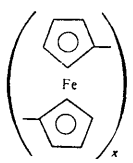
the main chain. The following reaction was carried out[367,368]



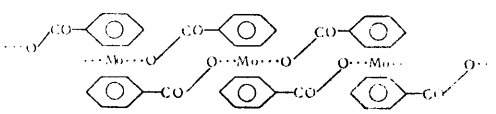
Other workers[368] have prepared polymers with the structure



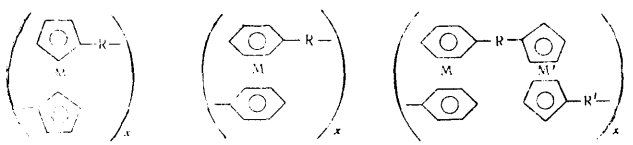
Recently Korshak *et al.*[369] have synthesised a polyferrocene with a molecular weight of ~2500



An interesting metallocene polymer is molybdenum(II) dibenzoate[370], which has been given the structure

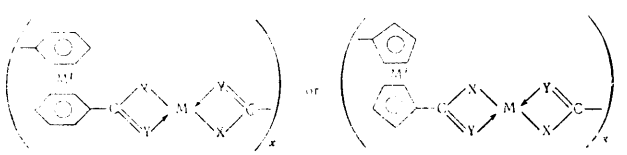


There are many as yet unused methods which could be applied to the synthesis of new types of polymers. It would be interesting to obtain polymers of the following types

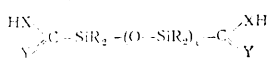


where R = alkyl or aryl group, O, S, NH, $R_2Si.O$, $R_2P:N$, etc.

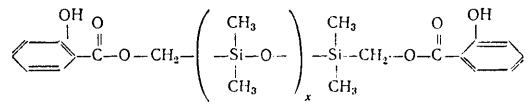
Another method would be addition of a chelatophoric group to a metallocene skeleton to obtain the corresponding chelate polymers



It would also be interesting to obtain chelate polymers in which the chelatophor was combined with a siloxane or other organo-elementary radical



The compound[371]



is of interest from this point of view.

Since chelate polymers combine the properties of organic and of inorganic polymers, and possess great thermal and chemical stability, it can be assumed that in the future they will play a special part in the production of new synthetic materials with special properties.

VI. FORMATION OF CO-ORDINATION POLYMERS IN SOLUTION

1. FORMATION IN WATER

It has long been known that ions in aqueous solutions are hydrated but a detailed study of aqueous solutions of metal salts has shown that the phenomena occurring in solution are very varied and complicated. Aqueous solutions of salts are often acidic or alkaline indicating that chemical interaction between metal ions and water molecules (hydrolysis) takes place in solution. Since modern research has shown that such reactions not infrequently involve the formation of polynuclear complexes which are co-ordination polymers, we will examine these phenomena below.

The first reaction which takes place when a salt is dissolved in water is hydration of the ions. In the case of a salt of a cation M^{p+}, having a co-ordination number of n with respect to water, and an anion A (A is assumed to be univalent in order to simplify the chemical equations), hydration can be represented by the equation

$$\underset{\text{crystalline salt}}{MA_p \cdot x\,H_2O} + n\,H_2O \rightleftarrows [M(H_2O)_n]^{p+}\,aq + p\,A^-\cdot aq \qquad (1)$$

This simple hydration reaction is followed by a number of secondary reactions, which to a large extent determine the macroscopic properties of the solution (pH, electrical conductivity, etc.). The water molecules co-ordinated with the central ion can lose hydrogen ions or can be replaced by OH^- ions from the solution:

$$[M(H_2O)_n]^{p+} + H_2O \rightleftarrows [M(H_2O)_{n-1}(OH)]^{(p-1)+} + H_3O^+ \qquad (2)$$

$$[M(H_2O)_n]^{p+} + OH^- \rightleftarrows [M(H_2O)_{n-1}(OH)]^{(p-1)+} + H_2O \qquad (3)$$

This reaction is favoured by a decrease in the hydrogen ion concentration. Complexes can be formed having one, two, or more hydroxyl groups co-ordinated to the central ion

$$[M(H_2O)_{n-1}(OH)]^{(p-1)+} + H_2O \rightleftarrows [M(H_2O)_{n-2}(OH)_2]^{(p-2)+} + H_3O^+. \qquad (4)$$

When their number is equal to the valency p of the metal, the hydroxide is precipitated.

These reactions are accompanied by an increase in the concentration of H^+ (or H_3O^+) ions in the solution, and can therefore be studied by the usual methods for determining hydrogen ion concentrations in solution.

We are especially interested in the formation of hydroxo complexes in solution, since they can be condensed to form polynuclear complexes[85-87], *i.e.* co-ordination polymers.

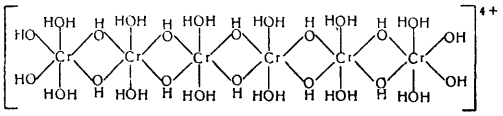
We shall therefore ignore, with Pokras[372,373], other possible reactions in aqueous solution and confine ourselves to the formation of these complexes, in which the OH groups act as bridges (reviewed by Basset[374]).

Hydrolytic co-ordination polymerisation. Reactions of this type can be represented by the following equations

$$[M(H_2O)_n]^{p+} + [M(H_2O)_{n-1}(OH)]^{(p-1)+} \rightleftarrows \rightleftarrows [(H_2O)_{n-1}M{-}OH{-}M(H_2O)_{n-1}]^{(2p-1)+} + H_2O. \quad (5)$$

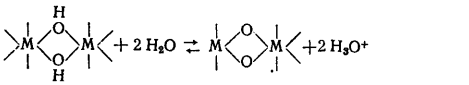
$$2[(H_2O)_{n-1}M(OH)]^{(p-1)+} \rightleftarrows [(H_2O)_{n-2}M\langle{}^{O}_{O}{}^{H}_{H}\rangle M(H_2O)_{n-2}]^{(2p-2)+} + 2H_2O. \quad (6)$$

These reactions can continue with the formation of co-ordination polymers of increased molecular weight containing 3, 4, 6, or more metal nuclei. Formation of complex polymers of the following type is possible[87]



We have seen that an increase in the concentration of OH^- ions in the solution favours reactions (2)–(4), which form the initial stages of the polymerisation process in solution. When a salt solution is made alkaline until the metal hydroxide separates, co-ordination polymers are present in the solution. Polymerisation develops as the solution is made alkaline, and is terminated by precipitation of the hydroxide, which is a high polymer (see section IV).

When a solution is allowed to stand, other reactions take place, which change the nature of the polymers, for example



This reaction is favoured by a decrease in the hydrogen ion concentration of the solution and by an increase in temperature.

These facts make it possible to understand the formation of hydroxides, oxides, and basic salts in aqueous solution and the polymeric structure of these compounds. These views on hydrolysis reactions (which are better termed hydrolytic co-ordination polymerisation reactions) have been expounded in papers by Stiasny[375,376], Thomas[377–380], Jander and Jahr[381–384], and later in the investigations of Hall and Eyring[385], Pokras[372,373], Kraus[386,387], Faucherre[388–391], Souchay[392,393], and Sillén and his collaborators[394–422]. The work carried out at Kungl. Tekniska Högskolan in Stockholm during the past ten years[387,394–419] has made a particularly great contribution towards elucidating the reactions occurring during the process of hydrolysis.

Sillén obtained general equations representing the process of hydrolysis, and worked out a mathematical method for calculating the composition and the degree of polymerisation of co-ordination polymers in solution. The method has been described in several reviews[387,394] and in the original papers[395–398].

Let us examine further some hydrolysis reactions. In order to simplify the reaction

$$M(H_2O)_6^{3+} + H_2O \rightleftarrows M(H_2O)_5(OH)^{2+} + H_3O^+,$$

we shall represent it as follows

$$M^{3+} + H_2O \rightleftarrows MOH^{2+} + H^+.$$

Study of a large number of metal ions has enabled metals to be classified as follows with respect to their behaviour on hydrolysis.

(a) Metals which form only mononuclear complexes on hydrolysis: Hg(I),[399] Hg(II),[400] Fe(II),[401] Tl(III),[402,403] Cd(II),[404] and Ag(I).[405,406] Thus, for example, Hg^{2+} forms $[HOHgOH_2]^+$ and [HOHgOH]. In Fe^{2+} solutions, $[FeOH]^+$ ions are formed, etc.

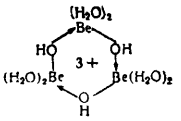
(b) Ions which on hydrolysis form dinuclear complexes or a limited number of complexes of definite degree of polymerisation: Be(II),[407] Cu(II),[408] Sn(II),[409] Fe(III),[403,410] Bi(III),[411,412] and Al(III).[403,413]

(c) Ions which on hydrolysis form continuous series of polynuclear complexes, of general formula

$$\{M[(OH)_pM]_x\}^{[(n-p)x+n]+},$$

where p is the number of OH groups, n the charge on the metal ion M^{n+}, and x the degree of polymerisation. This group includes the ions UO_2^{2+},[414] In(III),[403,415] Sc(III),[403,416] Th(IV),[417,418] and U(IV),[418,419]

Ions which form definite polynuclear complexes. Hydrolysis of the beryllium ion Be^{2+} has been studied potentiometrically using the quinhydrone and the calomel electrodes[394,407]. The main product of hydrolysis is the $Be_3(OH)_3^{3+}$ ion, accompanied by small amounts of the Be_2OH^{3+} ion and of $Be(OH)_2$.



It is supposed that beryllium has tetrahedral co-ordination, as in $Be(OH)_2$, involving water molecules: the $Be_3(OH)_3^{3+}$ cation has a cyclic structure. The main reaction in the hydrolysis of beryllium is

$$3Be^{2+} + 3H_2O \rightleftarrows Be_3(OH)_3^{3+} + 3H^+;\ \log K = -8.66 \pm 0.03$$

These workers assume that the compounds $BeOH(H_2O)_2 \cdot [HgCl_3]$, $Be(OH)(H_2O)_2[HgBr_3]$, and $Be_3(OH)_3(H_2O)_6[Hg_2I_7]$, described by Slavvo[423–425] contain polymeric cyclic cations similar structure.

The hydrolysis of the beryllium ion was also studied by Faucherre[388–390] and by Souchay[392,393] who assumed the existence of the $Be_4(OH)_4^{4+}$ ion in solution. Scandinavian workers[407] did not support this view. The $Be_2(OH)_2^{2+}$ ion, which was assumed by other workers[426,427] is also absent from solution.

In aqueous solution the Cu^{2+} ion forms only dinuclear complexes $Cu_2(OH)_2^{2+}$ on hydrolysis[408].

Hydrolysis of the Sn^{2+} ion yields mono-, di-, and trimeric complexes — $SnOH^+$, $Sn_2(OH)_2^{2+}$, and $Sn_3(OH)_4^{2+}$ — by the reactions[409]

$$3Sn^{2+} + 4H_2O \rightleftarrows Sn_3(OH)_4^{2+} + 4H^+;\ \log K = -6.77$$

$$2Sn^{2+} + 2H_2O \rightleftarrows Sn_2(OH)_2^{2+} + 2H^+;\ \log K = -4.45$$

$$Sn^{2+} + H_2O \rightleftarrows SnOH^+ + H^+;\ \log K = -3.9.$$

The following equilibria occur in the hydrolysis of the bismuth ion, Bi^{3+},[411,412]

$$Bi^{3+} + H_2O \rightleftarrows BiOH^{2+} + H^+;\ \log K = -1.58 \pm 0.02$$
$$6Bi^{3+} + 12H_2O \rightleftarrows Bi_6(OH)_{12}^{6+} + 12H^+;\ \log K = 0.330 \pm 0.005.$$

The main reaction product is the $Bi_6(OH)_{12}^{6+}$ (or $Bi_6O_6^{6+}$) ion. A continuous series of complexes $\{Bi[(OH)_2Bi]_n\}^{3+n}$, as seemed possible earlier, is not formed[420].

These polycations having six bismuth atoms are hydrolysed with the formation of a nonanuclear cation[412]:

$$1.5\,Bi_6(OH)_{12}^{6+} + 2H_2O \rightleftarrows Bi_9(OH)_{20}^{7+} + 2H^+;\ \log K = -3.5 \pm 0.1$$
$$Bi_9(OH)_{20}^{7+} + H_2O \rightleftarrows Bi_9(OH)_{21}^{6+} + H^+;\ \log K = -3.2 \pm 0.2.$$

The structure of these complexes is unknown

The presence of polynuclear bismuth complexes in solution has been demonstrated by various methods. The ions $Bi_4O_4^{4+}$, $Bi_5O_5^{5+}$, and $Bi_6O_6^{6+}$ have been detected photometrically[428]. It was not possible with the ultracentrifuge to establish whether the complexes contain five or six bismuth atoms[429].

Tobias[430] considers that hydrolysis of Bi^{3+} proceeds according to the equations

$$6Bi^{3+} + 6H_2O \rightleftarrows Bi_6O_6^{6+} + 12H^+;\ Bi_6O_6^{6+} + 3H_2O \rightleftarrows Bi_6O_6(OH)_3^{3+} + 3H^+.$$

Hydrolysis of ferric iron yields only mono- and di-nuclear complexes[403,410]

$$Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+;\ \log K = -3.05$$
$$FeOH^{2+} + H_2O \rightleftarrows Fe(OH)_2^+ + H^+;\ \log K = -3.26$$
$$2Fe^{3+} + 2H_2O \rightleftarrows Fe_2(OH)_2^{4+} + 2H^+;\ \log K = -2.91$$

When hydrolysis is continued, the hydroxide is formed.

Hydrolysis of the Pb^{2+} ion gives the following products[421]

$$Pb^{2+} + H_2O \rightleftarrows PbOH^+ + H^+$$
$$4Pb^{2+} + 4H_2O \rightleftarrows Pb_4(OH)_4^{4+} + 4H^+$$
$$3Pb^{2+} + 4H_2O \rightleftarrows Pb_3(OH)_4^{2+} + 4H^+$$
$$6Pb^{2+} + 8H_2O \rightleftarrows Pb_6(OH)_8^{4+} + 8H^+$$

Pedersen[431] proved that the ions Pb_2OH^{3+} and $Pb_4(OH)_4^{4+}$ are formed, and Faucherre[432] considers that hydrolysis of Pb^{2+} gives $Pb_4(OH)_4^{4+}$, $Pb_9(OH)_{12}^{6+}$, and $PbOH^+$.

The hydrolysis of the Al^{3+} ion has been investigated by various workers, who have emphasised the presence of polynuclear complexes in the solution. Brosset, Biedermann, and Sillén[403,413] were unable to determine exactly whether complexes having definite degrees of polymerisation or continuous series of polymers were formed in solution. In acid medium ions having the composition $Al[(OH)_5Al_2]^{(3+x)+}$ are formed, and in alkaline medium $[Al(OH)_3]_x(OH)^-$ ions; it cannot be said whether x assumes a series of values or only certain values. Formation of the complex $Al_6(OH)_{15}^{3+}$, for which a cyclic structure (Fig. 23) is suggested, is most probable in acid medium. This agrees with results obtained by Kohlschütter and Hantelman[433], who found cryoscopically that the size of the molecule in a solution containing Al : OH = 1 : 1.5 corresponds to six Al atoms, *i.e.* to the $Al_6(OH)_{15}^{3+}$ ion.

The complex ions $Al_2(OH)_2^{4+}$ and $Al_3(OH)_6^{3+}$ are not the chief products of hydrolysis, even if they are formed in solution. The presence in solution of complexes having higher degrees of polymerisation is not excluded.

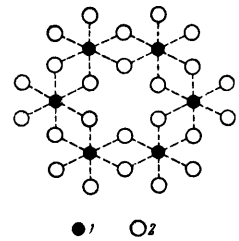


Fig. 23. Structure of hexanuclear complex $Al_6(OH)_{15}^{3+}$ aq complex: 1) Al; 2) OH or H_2O.

Ions which form continuous series of polymers. Ions of several metals form polynuclear complexes of indefinite degree of polymerisation on hydrolysis. Continuous series of polymers are formed, with the general formula $M[(HO)_pM]_x$, where x = 1, 2, 3, 4, 5, 6, ...

Hydrolysis of the In^{3+} ion involves the equilibria[403,415]

$$In^{3+} + 2H_2O + In^{3+} \rightleftarrows In(OH)_2In^{4+} + 2H^+;\ \log K = -5.21$$
$$In[(HO)_2In]_x^{x+2} + 2H_2O + In^{3+} \rightleftarrows In[(OH)_2In]_{x+1}^{x+4} + 2H^+;\ \log K = -4.69$$

the general equation being

$$(x+1)In^{3+} + 2xH_2O \rightleftarrows In[(OH)_2In]_x^{3+x} + 2xH^+.$$

These polymers probably have a linear structure, since X-ray analysis has shown[214,434] that basic salts of indium contain linear polymeric ions $In(OIn)_x^{(x+3)+}$.

Hydrolysis of the Sc^{3+} ion[403,416] is represented by the general equation

$$(x+1)\,Sc^{3+} + 2xH_2O \rightleftarrows Sc[(OH)_2Sc]_x^{x+3} + 2xH^+;\ \log K = 0.70 - 0.87x$$

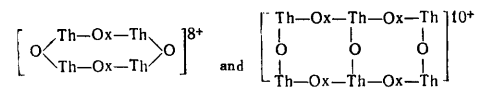
The solution contains species having x = 1, 2, 3, such as, for example, $Sc(OH)^{2+}$, $Sc(OH)_2^+$, $Sc_2(OH)_2^{4+}$, and $Sc_3(OH)_4^{5+}$, as well as higher polymers. The degree of polymerisation increases step by step, according to the equation

$$Sc[(OH)_2Sc]_x^{x+3} + 2H_2O + Sc^{3+} \rightleftarrows Sc[(OH)_2Sc]_{x+1}^{x+4} + 2H^+$$

New data[417,418] on the hydrolysis of thorium Th^{4+} indicate the formation of a series of complexes $Th[(OH)_3Th]_x$, where x = 1, 2, 3, ..., 6, and above. Early work showed that formation of $Th_4O_4^{8+}$ ions takes place, but other workers[435] point to the formation of the ions $Th(OH)_2^{2+}$, $Th_2(OH)_2^{6+}$, and $Th_5(OH)_{12}^{8+}$. The $Th_2(OH)_2^{6+}$ ion was detected by Hietanen and Sillen[436]. A linear structure is suggested for the polycations formed on hydrolysis: $Th\overset{O}{\underset{OH}{}}Th\overset{O}{\underset{OH}{}}Th\overset{O}{\underset{OH}{}}...Th\overset{O}{\underset{OH}{}}Th$ or $Th(\overset{O}{\underset{OH}{}}Th)_x$. This hypothesis is based on X-ray analysis[422], which showed the presence of $Th[\overset{O}{\underset{OH}{}}Th]_x^{(4+x)+}$ chains in the structures of the basic sulphate and the basic chromate of thorium (SO_4ThOH and CrO_4ThOH), as well as on an electron-diffraction study[437,438] of thorium hydroxide.

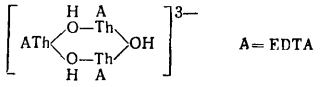
It is interesting that polynuclear thorium complexes containing Th–O–Th bridges are also formed with oxalic acid[439].

The ions $[Th_4O_2(Ox)_2]^{8+}$ and $[Th_6O_3(Ox)_4]^{10+}$, where Ox = $= (COO)_2^{2-}$, were detected, having the possible structure



Water molecules, of course, are co-ordinated to the thorium atoms.

Chelates of thorium with ethylenediaminetetra-acetic acid (EDTA) hydrolyse with the formation of a cyclic trimer [440]



A = EDTA

Hydrolysis of the U^{4+} ion [418,419] is similar to that of the Th^{4+} ion. A mononuclear complex is formed first

$$U^{4+} + H_2O \rightleftarrows UOH^{3+} + H^+,$$

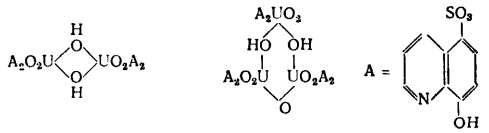
and then the polymers

$$(x+1)\,U^{4+} + 3xH_2O \rightleftarrows U[(OH)_3U]_x^{(4+x)+} + 3xH^+.$$

These polymers apparently have a linear structure $U[{}^{O}_{OH}U]_x^{(4+x)+}$, similar to the compound $U(OH)_2SO_4$, studied by X-ray diffraction [441], which contains $[U(OH)_2]_x^{2x+}$ infinite chains. In the compound $U_6O_4(OH)_4(SO_4)_6$ X-ray analysis has detected [442] the presence of discrete $U_6O_4(OH)_4^{12+}$ ions.

Hydrolysis of the UO_2^{2+} ion results in the formation of a series of polymers having the composition $UO_2[(OH)_2UO_2]_x^{(2+x)+}$ (or $UO_2[OUO_2]_x^{(2+x)+}$). [414] It is suggested that the structure of these complexes is based on layers of the given composition in which the UO_2 group forms four U–O co-ordinate links, as in the structure of $BaUO_2O_2$ [443] and $CaUO_2O_2$. [444] Recent work has shown [445] the formation of cations having the composition $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_4^{2+}$.

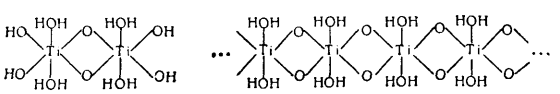
Co-ordination polymers are formed by an analogous mechanism in solutions of several uranyl chelates [446]. Thus dimers and trimers of the following structure are formed [446]



The precise structure of such trimers is still unknown.

The literature contains data on the hydrolysis of other ions, but the results are not yet sufficiently convincing, and the precise composition of the hydrolysis products is unknown. Polymerisation phenomena have been observed in solutions of cerium salts [447,448], in which dimers, trimers, and polymers are present. X-Ray patterns have shown [449] that the basic salt $CeOSO_4.H_2O$ contains macromolecular Ce–O chains, while the salt $Ce_6O_4(OH)_4(SO_4)_6$ is made up of $Ce_6O_4(OH)_4^{12+}$ ions.

Other workers have shown the presence of polymeric complexes in solutions of titanium salts. Thus the Ti^{4+} ion in solution forms polymeric complexes of the type [450]



It has been shown spectrophotometrically [451] that solutions of peroxotitanic acid are also polymeric. The presence of macromolecular Ti–O chains in the structure of $TiOSO_4.H_2O$ has been established by means of X-rays [452].

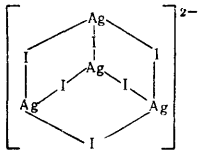
The zirconium ion Zr^{4+} is also able to form polymers [453]. The ions $Zr_3(OH)_4^{8+}$ and $Zr_4(OH)_8^{8+}$ exist, and higher polymers are probable. This agrees with Lundgren's X-ray results [454] showing that basic zirconium chromate contains $[Zr_4(OH)_6.CrO_4]_x^{8x+}$ endless chains containing Zr–OH–Zr co-ordinate links. The ions $Zr_4(OH)_8(H_2O)_{16}^{8+}$ have been detected [455] in both $ZrOCl_2.8H_2O$ and $ZrOBr_2.8H_2O$. Oxalate polymers $Zr_nx.[(COO)_2]_x$ ($n = 2, 3, 4, \ldots$) have been discovered [456]. Some chelate compounds of zirconium are also polymeric [457,458].

The hydrolytic polymerisation of the chromic ion, Cr^{3+}, has been widely studied [375,376,459–464] and formation of polynuclear complexes of high molecular weight is possible. The Cr^{3+} ion can probably form a continuous series of polymers on hydrolysis.

Polycations of high molecular weight are also formed in the hydrolysis of salts of magnesium Mg(II), [383] zinc, [384] and plutonium [456].

In all these cases it is unknown whether continuous series of complexes or complexes having a definite degree of polymerisation are formed and it would be very useful to apply Sillén's method to an investigation of the hydrolysis of these ions.

Other ligands besides the OH ion are able to form polymeric, polynuclear complexes in solution. Interesting work by Nilssen [466] has shown that the complexes $Ag_2(S_2O_3)_4^{6-}$, $Ag_3(S_2O_3)_5^{7-}$, and $Ag_6(S_2O_3)_8^{10-}$ are formed having co-ordinate links between the silver ions and the thiosulphate groups. In the $Ag_4I_6^{2-}$ ion the Ag and I atoms occupy positions corresponding to a urotropine type of structure [467]



Sillén's method can probably be used also with multivalent ligands: it would be useful to study systems containing metal ions together with these ligands both in aqueous solution and in organic solvents. Most precipitation reactions are probably preceded by the formation in solution of polymeric (polynuclear) complex ions. The formation of sparingly soluble sulphides and other precipitation reactions employed in analytical chemistry would merit careful study from this angle.

We see from this section that the formation of polymeric complexes in solution is associated with the formation of basic salts. Study of the latter is therefore of great interest in connection with the chemistry of co-ordination polymers; existing results may give an impetus to such investigations. In addition to work cited, note must be taken also of that of Feitknecht [266–271,468], who studied a number of basic salts, which X-ray studies showed to be macromolecular co-ordination compounds [468]:

$[Cu_2(OH)_3NO_3]_\infty N$ — two-dimensional lattice of single layers
$[Zn_3(OH)_6Zn_2Cl_2H_2O]\,N$ — two-dimensional lattice of double layers
$[Mg_4(OH)_8(H_2O)_4ClH_2O]_\infty K$ — linear macromolecular structure
$[Cu_2(OH)_3Cl]_\infty G$ — three-dimensional macromolecular structure

2. Formation in Liquid Ammonia

We have seen that in aqua systems the OH^- ions can replace water molecules in the solvated complex $[M(H_2O)_n]$ with the formation of polynuclear complexes. Several contemporary investigations showed that reactions of complex ammines $[M(NH_3)_6]^{p+}$ with alkali metal amides MNH_2 in liquid ammonia involve reactions analogous to those occurring in aqueous solutions

$$[M(NH_3)_n]X_p + nNH_2^- \rightleftarrows [M(NH_3)_n](NH_2)_p + pX^-$$
$$\downarrow\uparrow$$
$$[M(NH_3)_{n-p}(NH_2)_p] + pNH_3$$

Formation of amido complexes may be accompanied by the formation of polymers with elimination of NH_3 groups from the complex, co-ordination unsaturation being met by a bifunctional group, NH_2, acting as a bridge

$$2[M(NH_3)_{n-1}(NH_2)]^{(p-1)+} \xrightarrow{-NH_3} \left[(H_3N)_{n-2}M\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}M(NH_3)_{n-2}\right]^{(2p-2)+} + 2NH_3$$

If the concentration of NH_2^- ions increases, macromolecular complexes are formed in the solution

$$[M(NH_3)_n] \xrightarrow[-NH_3]{+NH_2^-} \left[\begin{smallmatrix}H_3N & NH_3 & H_3N & NH_3\\ & M & -NH_2- & M \\ H_3N & NH_3 & H_3N & NH_3\end{smallmatrix}-NH_2-\right]_x \xrightarrow[-NH_3]{+NH_2^-} \left[\begin{smallmatrix}NH_3 & H_2 & NH_3 & H_2\\ & M & -NH_2- & M \\ NH_3 & H_2 & NH_3 & H_2\end{smallmatrix}-NH_2-\right]_x \xrightarrow[-NH_3]{+NH_2^-} \left[\begin{smallmatrix}H_2 & & H_2\\ & M-NH_2-M & \\ H_2 & & H_2\end{smallmatrix}-NH_2-\right]_x$$

Schmitz-Dumont and his coworkers [19,469-471] obtained co-ordination polymers from metal amides, hydroxoamides, μ-oxoamides, and alkoxoamides using such reactions.

Treatment of $[Cr(NH_3)_6](NO_3)_3$ and $[Co(NH_3)_6](NO_3)_3$ with potassamide KNH_2 yielded the corresponding amides $Cr(NH_2)_3$ and $Co(NH_2)_3$, in which Cr and Co retain a co-ordination number of 6.[472] Schmitz-Dumont ascribed a linear polymeric structure to these compounds

$$\left[\begin{smallmatrix}H_3N & & NH_2 & & NH_3\\ H_3N & -Cr- & NH_2 & -Cr- & NH_3\\ H_3N & & NH_2 & & NH_3\end{smallmatrix}\right]_x \qquad \left[\begin{smallmatrix}H_3N & & NH_2 & & NH_3\\ H_3N & -Co- & NH_2 & -Co- & NH_3\\ H_3N & & NH_2 & & NH_3\end{smallmatrix}\right]_x$$

In the reviewer's opinion a two-dimensional structure, similar to that of the hydroxides of tervalent metals (Fig. 21), is more probable. These complexes are formed by the following mechanism[473]

$$2[Co(NH_3)_6](NO_3)_3 \xrightarrow{+2KNH_2} [(H_3N)_4Co(NH_2)NH_2Co(NH_3)_4]^{2+} + 2NH_3$$

$$\xrightarrow[+NO_3^-]{+3NH_2^-} \left[\begin{smallmatrix}NH_2 & & NH_2\\ -Co- & NH_2 & -Co- \\ NH_3 & NO_2 & NH_2\end{smallmatrix}\right]_x \xrightarrow[-NO_3^-]{+NH_2^-} \left[\begin{smallmatrix}NH_2 & & NH_2\\ -Co- & NH_2 & -Co- \\ NH_2 & & NH_2\end{smallmatrix}\right]_x$$

Like the corresponding hydroxides, the amides of chromium and cobalt have amphoteric properties. Ammonium salts NH_4X, which in liquid ammonia are acids, react with amides, rupturing some of the amide bridges ($-NH_2-$) with the formation of *macromolecular cations*, and finally mononuclear complexes

$$\left[\begin{smallmatrix}NH_2 & & NH_2\\ -Co- & NH_2 & -Co- \\ NH_2 & & NH_2\end{smallmatrix}\right]_x \xrightarrow{+2xNH_4^+} \left[\begin{smallmatrix}NH_3 & NH_2 & NH_3 & NH_2\\ -Co- & NH_2 & -Co- \\ NH_3 & & NH_3 & \end{smallmatrix}\right]^{2x+}_x \xrightarrow{+2xNH_4^+} \left[\begin{smallmatrix}H_3N & NH_3 & H_3N & NH_3\\ -Co- & NH_2 & -Co- \\ H_3N & NH_3 & H_3N & NH_3\end{smallmatrix}\right]^{4x+}_x \xrightarrow{+2xNH_4^+} 2x[Co(NH_3)_6]^{3+}$$

Potassamide is a base in liquid ammonia; it reacts with amides, rupturing NH_2 bridges with the formation of *macromolecular anions*

$$\left[\begin{smallmatrix}NH_2 & & NH_2\\ -Co- & NH_2 & -Co- \\ NH_2 & & NH_2\end{smallmatrix}\right]_x \xrightarrow{+2xNH_2^-} \left[\begin{smallmatrix}NH_2 & NH_2 & NH_2 & NH_2\\ -Co- & NH_2 & -Co- \\ NH_2 & & NH_2 & \end{smallmatrix}\right]^{2x-}_x \xrightarrow{-NH_3} \left[\begin{smallmatrix}(-)NH & & (-)NH\\ -Co- & NH_2 & -Co- \\ NH_2 & & NH_2\end{smallmatrix}\right]^{2x-}_x$$

The latter reaction involves elimination of ammonia from two neighbouring NH_2 groups

$$\left[\begin{smallmatrix}NH_2 & H_2N\\ -Co- & NH_2 & -Co- \\ NH_2 & & \end{smallmatrix}\right] \xrightarrow{-NH_3} \left[\begin{smallmatrix}(-)NH & \\ -Co- & NH_2 & -Co- \\ NH_2 & & \end{smallmatrix}\right]$$

In this way a compound of the following structure is formed[474]

$$\left[\begin{smallmatrix}H & (-) & K^+ & H & (-) & K^+\\ & N & & & N & \\ -Co- & NH_2 & -Co- & NH_2 & & \\ & N & & & & \\ H & (-) & K^+ & & & \end{smallmatrix}\right]_x$$

Thermal decomposition of this compound leads to the polymer $(Co_2N_3K_3)_x$. The reactions with chromium amide are similar.

Polymeric amides have also been obtained of titanium[475], vanadium[476], and thorium[477]

$$x[Ti(SCN)_6]K_2 \xrightarrow[-KSCN]{+KNH_2} [Ti(NH_2)_4K]_x \xrightarrow{-NH_3} [Ti(NH)_2K]_x$$

$$x[V(SCN)_6]K_3 \xrightarrow[-KSCN]{+KNH_2} [V(NH_2)_4K]_x \xrightarrow{-NH_3} [V(NH)_2K]_x$$

$$x[Th(NO_3)_6]K_2 \xrightarrow[-KNO_3\ -NH_3]{+KNH_2} [Th(NH_2)_2NH_2K]_x$$

$$x[Th(NO_3)_6]K_2 \rightarrow [Th(NH_2)_2NH]_x \xrightarrow[-NH_3]{50^\circ} [Th_2(NH)_3(NH_2)_2]_x \rightarrow$$

$$\xrightarrow[-NH_3]{100^\circ} [Th(NH)_2]_x \xrightarrow{130^\circ} Th_3N_4$$

All these compounds are polymers in which the metal atoms are linked by NH_2, NH, or N groups. Polymerisation of these compounds is caused by the tendency of the metal to maintain a co-ordination number of 6.

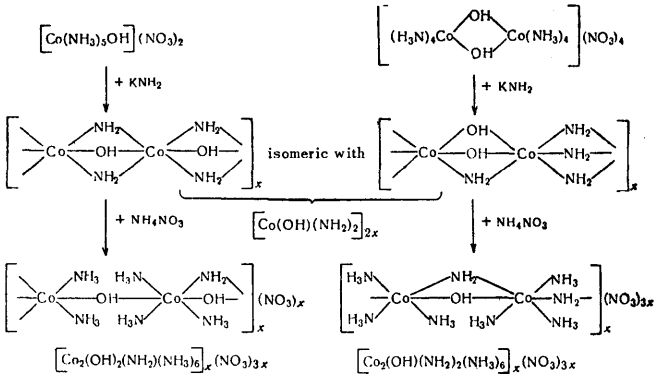
A linear uranyl amide has also been obtained[478]

$$K[UO_2(NO_3)_3] + 3KNH_2 \rightarrow \frac{1}{x}\left[\begin{smallmatrix}O & & O & \\ -U- & NH_2 & -U- & NH_2 \\ O & & O & \end{smallmatrix}\right]_x + 3KNO_3$$

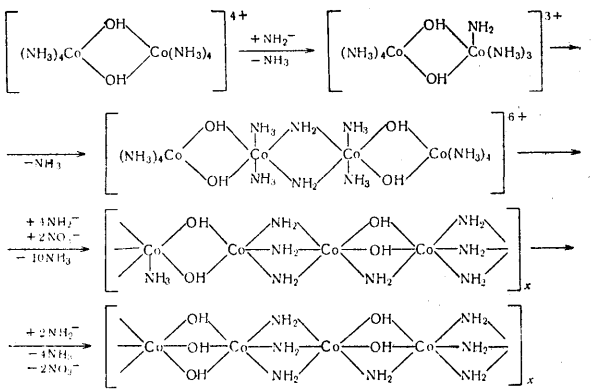
This compound possesses amphoteric properties, forming $UO_2(NH_3)_2I_2$ with ammonium iodide, and $[UO_2(NH_2)_2K_2]$ with potassamide. Thermal decomposition yields the

polymer $[(UO_2)_3N_4K_6]_x$. A number of complexes containing both OH and NH_2 bridges have been prepared.

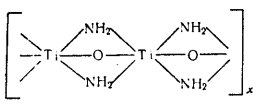
The action of potassamide on $[Co(NH_3)_5OH](NO_3)_2$ and $[(NH_3)_4Co(OH)_2.Co(NH_3)_4](NO_3)_4$ in liquid ammonia yields [473] two isomers having the formula $[Co(NH_2)_2(OH)]_x$. This is probably the first case of isomerism in the chemistry of co-ordination polymers. Both isomers are amphoteric. A scheme for the formation of these isomers, their structure, and their reaction with NH_4NO_3 are given below



The mechanism of the reaction was elucidated by identifying intermediate products.

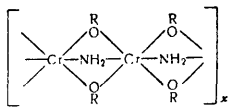


Among oxoamides only titanylamide is known [479], having the structure



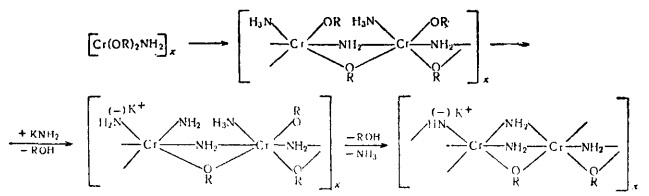
The hydrogen atom of the OH bridges can be replaced by organic radicals, yielding amidoalkoxides or alkoxoamides [480] $[M(OR)(NH_2)_2]_x$ and $[M(OR)_2NH_2]_x$, where M = Co, Cr.

Reaction among $[Cr(NH_3)_6](NO_3)_3$, alcohols, and potassamide in liquid ammonia yields [481,482] amphoteric compounds $[Cr(OR)_2NH_2]_x$

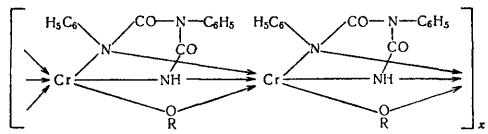


where R = $CH_2.C_6H_5$ [481] or C_6H_5. [482]

With ammonium iodide these compounds are converted into $[Cr(NH_3)_6]I_3$, and with potassamide several bridges are ruptured with the formation of a new polymer



Treatment of $[Cr(OR)_2NH_2]_x$ compounds with phenylisocyanate yields polymers of the structure



A study has been made [480] of cobalt amidoalkoxides $[Co(NH_2)_2OR]_x$, where R = CH_3, C_2H_5.

In liquid ammonia the compound KPH_2 reacts similarly to potassamide, forming polymers. The compounds $[Co(PH_2)_3]_x$ and $[Ni(PH_2)_2]_x$ have been obtained [483], as well as other compounds containing $-NH_2-$ and $-PH_2-$ groups.

VII. PROSPECTS AND OUTSTANDING PROBLEMS

This review of co-ordination polymers has shown the special role of co-ordinate bonds in macromolecular chemistry. The chemistry of co-ordination polymers is an interesting branch of modern inorganic chemistry and of the chemistry of complex compounds, offering new methods of synthesis of macromolecular compounds.

It is evident from the present survey that research in this field is only in its initial stage of development. It is necessary to continue and extend investigations into the following problems in the chemistry of co-ordination polymers:

(a) A study of the structure of inorganic compounds which are potentially polymeric, in particular derivatives of transition metals such a cyanides, sulphides, halides thiocyanates, complex compounds having an abnormal co-ordination number, basic salts, metal amides, chelate compounds, etc. For this purpose wide use must be made of X-ray and electron diffraction, spectroscopic, and other physical methods.

(b) Determination of the molecular weight of inorganic compounds and their organic derivatives under various conditions, mainly in inert solvents, in which the phenomena of co-ordinate association (*i.e.* polymerisation) take place, or in the vapour phase (when possible).

(c) Synthesis of new co-ordination polymers, metallocene polymers are of great interest in this connection.

(d) Physicochemical study of co-ordination polymers — mechanism and kinetics of formation and decomposition, equilibrium in solution, determination of thermodynamic constants, etc.

(e) Theoretical study of co-ordination polymers. It would be interesting to study the nature of the chemical bond in

these polymers, many-centre many-electron bonds probably playing a great part here. The stereochemistry of these polymers is especially interesting.

(f) The discovery of new opportunities for their practical application. These compounds are of interest from the point of view of producing new materials having special properties, for example, increased thermal stability, and semiconducting, dielectric, catalytic, and other properties.

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I. INTRODUCTION

Most of the therapeutically valuable alkaloids have synthetic substitutes containing the same structural elements. They are simpler in structure and are manufactured on an industrial scale. At present the synthetic antimalarials (atebrin, bigumal), anaesthetics (promedol), local anaesthetics (novocaine), and other synthetic drugs are often superior in their properties to the natural ones and are favoured in medical practice.

In 1952, from the plant *Rauwolfia serpentina*, Müller, Schlittler, and Bein[1] isolated reserpine (I), an alkaloid of the indole group, with a sedative and hypotensive action.

The remarkable activity of reserpine and its wide applicability in medicine[2,3] for the treatment of hypertonia and mental diseases has attracted considerable interest. Its structure was established[4] in 1954, and in 1956 Woodward and his collaborators[5] carried out its complete synthesis.

Studies of the correlation between the structure of reserpine and its pharmacological activity were started in 1954. Yakhontov[6] discussed this subject in his review of the alkaloids from *Rauwolfia*.

A good deal of work is being done at present in an attempt to find simple analogues of reserpine. All efforts to synthesise a reserpine substitute are directed towards the preparation of various fragments of the reserpine molecule, *viz.* the derivatives of yohimbine, β-carboline, indole, isoquinoline, cyclohexanol, and trimethoxybenzoic acid.

This review discusses all the attempts made so far to synthesise simple analogues of reserpine.

II. EFFECT OF STRUCTURAL CHANGES IN THE RESERPINE MOLECULE ON ITS BIOLOGICAL ACTIVITY

The pharmacological study of the alkaloids from *Rauwolfia* led to the discovery of an interesting type of action on the central nervous system, the so-called reserpine-like action, which is at once sedative and hypotensive.

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