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Complexes of natural carbohydrates with metal cations

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Abstract. Data on the interaction of natural carbohydrates (mono-, oligo-, and poly-saccharides, amino sugars, and natural organic acids of carbohydrate origin) with metal cations are surveyed and described systematically. The structural diversity of carbohydrate metal complexes, caused by some specific features of carbohydrates as ligands, is demonstrated. The influence of complex formation on the chemical properties of carbohydrates is discussed. It is shown that the formation of metal complexes plays an important role in the configurational and conformational analysis of carbohydrates. The practical significance of the coordination interaction in the series of carbohydrate ligands is demonstrated. The bibliography includes 571 references.

I. Introduction

Metal complexes of natural carbohydrates have been attracting interest for many years because these compounds participate in vitally important processes; they are used for configurational and conformational analysis, determination, and separation of sugars. According to our estimates, at least 1000 studies discussing various aspects of complex formation between metal ions and natural carbohydrates (mono-, oligo-, and polysaccharides, amino sugars, their polymers, carbohydrate carboxylic acids, natural organic acids of the carbohydrate origin, and cyclic and acyclic polyols) have been published.[2] However, even the most comprehensive monographs dealing with the chemistry of coordination compounds [1] or carbohydrates [2] do not consider carbohydrates to be ligands. Several reviews published to date [3 – 16] cover only some aspects of this topic.

The purpose of this review is to survey as fully as possible the published data on the known complexes of natural carbohydrates with metal cations; therefore it includes both recent studies and the most important of early studies. The formation of complexes by nucleosides and nucleotides is beyond the scope of the review, because the carbohydrate fragments of these molecules normally do not participate in the coordination of metals. Moreover, this aspect has been the subject of numerous reviews and monographs (see, for example, Refs 17, 18). The few known examples in which the carbohydrate fragments of nucleotides and nucleosides are involved in the formation of complexes with metals are presented in Section IV.

Data on the formation of metal complexes in the series of natural carbohydrates are mainly discussed in relation to reliably established structures. The information is classified according to the type of carbohydrates. Within each type, metal cations are arranged in accordance with their electronic configuration (*s*-, *p*-, *d*-, and *f*-metals) and their position in the Mendeleev Periodic Table.

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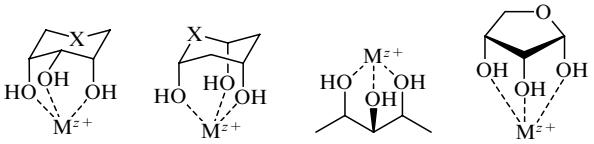
II. Complexes of mono-, oligo-, and polysaccharides and their derivatives

1. Ionic complexes with *s*-metal cations

The first review [6] on the complexation of carbohydrates with *s*-metal compounds was published in 1966, and now it is only of historical interest. X-Ray diffraction data for metal complexes of this type can be found in a number of reviews (see, for example, Refs 19 – 23) including a review devoted to saccharose.[24] The data on the structures of solid ionic metal complexes obtained up to the middle of 1978 are surveyed most fully in the review by Poonia and Bajai.[11]

A systematic study of the structures of complexes of monosaccharides with *s*-metal cations in aqueous solutions carried out by Angyal [7, 8, 12] has demonstrated that complexes of 1 : 1 composition predominate. In the case of cyclic forms of ligands, the most stable complexes are those with the axial – equatorial – axial orientation of three consecutively located hydroxyl groups in the ligand (complex **1a**, the first Angyal rule) or those with the energetically unfavourable triaxial orientation of these groups (complex **1b**, the second Angyal rule). Acyclic derivatives obey the first Angyal rule (complex **2**), while furanoses obey the second rule (complex **3** with a quasiaxial orientation of the hydroxyl groups). These rules were derived using ^{1}H NMR spectroscopy, *i.e.* they were first formulated for relatively con-

centrated solutions. Their validity for dilute solutions was confirmed later by calorimetry.[25]



1a **1b** **2** **3**

X = O, CHOH; z = 1, 2.

Complex formation can shift the position of a tautomeric or conformational equilibrium for a ligand in an aqueous solution.[7,8,12] The stability constants of the complexes are relatively low (0.1–6.0).[7,8,12,16,26–30] The ability of *s*-metals to form complexes with disaccharides is less pronounced than that for monosaccharides.[31,32] Evidently, this is due to the higher conformation rigidity of the former. The stability constants of *s*-metal complexes of monosaccharide carboxylic acids are only an order of magnitude larger.[33–35] Thus, this complexation is very weak although fairly stereospecific. In solvents that are less polar than water (methanol, acetone, dioxane), these complexes are more stable because there are no water molecules to compete with the ligands for coordination to metal cations.[36]

The formation of these ionic metal complexes is usually regarded[7,11] as consecutive substitution of water molecules in the hydration shell of a metal ion by hydroxyl groups of the ligand, the optimum number of these groups (three) being determined by the Angyal rules. During the formation of solid complexes, this process is continued with participation of other ligand molecules, but does not go to completion. The data for a number of solid complexes of sugars with *s*-metal salts obtained by X-ray diffraction analysis[10,15,37–45] and by IR spectroscopy[46–53] permit the following general conclusions.

1. Carbohydrates act most often as bidentate ligands coordinated through vicinal diol fragments, which can be different in identical ligands. In some cases, the formation of a complex ends with incorporation of a monodentate ligand.[38,54] Complexes of acyclic aldonic acids can contain only monodentate ligands.[55,56]

2. Since there are only three known examples[57–59] of tridentate coordination of cyclic ligands conforming to the first Angyal rule, one can conclude that this rule is not necessary for solid ionic metal complexes of sugars. At the same time, sugars containing no vicinal hydroxyl groups characterised by an axial–equatorial–axial arrangement (α-D-glucopyranose **4a**) do not form complexes of this type.[11]

3. As a rule, these complexes are crystal hydrates in which all water molecules are coordinated to metal ions.

4. The complexes normally contain two or three ligands, although in some cases they contain only one ligand.[60,61] In the case of acyclic carbohydrate derivatives, the number of ligands increases to four[62,63] or even to six.[55,56] The number of ligands in less studied disaccharide complexes is two[44,64–67] or one.[68]

5. After complexation, the coordination number of the metal remains approximately the same as that in the first coordination sphere of the initial hydration shell of the metal cation; most frequently it is equal to eight (square antiprism), six (octahedron), seven (pentagonal bipyramid), or nine (three-cap trigonal prism).[13] The coordination polyhedra formed by calcium(II) ions are especially diverse.[39]

6. In the majority of complexes of carbohydrate carboxylic acids, a metal ion is coordinated to an oxygen atom of the carboxyl group and to the hydroxyl group in the α-position (α-type coordination[69]). Only in complexes with these ligands, can the ring oxygen atom be involved in coordination.[70]

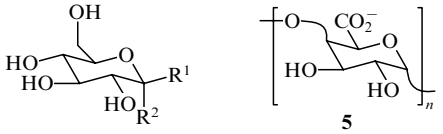
7. Conformational changes in the ligand following the complex formation are typical of neutral carbohydrates and normally reduce to the change in the conformation of the coordinated primary hydroxyl group[44] or in the dihedral angle between the coordinated vicinal hydroxyl groups.[11] In anionic ligands, coordination mostly involves the carboxyl group; this substantially decreases electrostatic interactions between the hydroxyl groups responsible for the conformational changes.[11,64]

8. The cation and the anion of the metal salt are coordinated separately and, thus, they are relatively far removed from each other. There is only one known example[45] of formation of a complex in which a salt occurs as a contact ion pair.

9. The majority of the complexes studied are calcium compounds, while the smallest number is represented by magnesium compounds. The particular affinity for calcium is apparently a fundamental property of carbohydrates.[11,39]

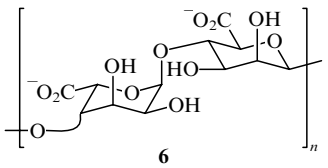
As regards polysaccharides, complexes of neutral polysaccharides with *s*-metal cations have been relatively little studied to date. Judging by X-ray diffraction data, the K^+ and Br^- ions in the complex of potassium bromide with amylose (a polymer of α-1,4-linked α-D-glucopyranose **4a**) are coordinated alternately in the cavity of the helix-like polymer chain.[71] It has been noted[72] that cellulose (a polymer of β-1,4-linked β-D-glucopyranose **4b**) only weakly binds Ca^{2+} ions. It was established unambiguously[73] that reaction of cellulose with alkali metal hydroxides gives inclusion compounds containing metal ions between the planes of the cellulose crystal lattice rather than the corresponding alkoxides.[74] The formation of alkoxides was denied even for monosaccharides[75] and disaccharides;[75,76] in these cases, the formation of adducts of the type $RO^+H(M)OH^-$ stabilised by hydrogen bonds between the neighbouring hydroxyl groups was postulated.

A more detailed study[77] has been devoted to the formation of complexes of *s*-metal cations with a number of anionic polysaccharides, first of all, with pectate **5** (α-1,4-linked poly-α-D-galactopyranosuronate), alginate **6** (a polymer consisting of α-1,4-linked disaccharides formed by the α-L-gulopyranosuronic and β-D-mannopyranosuronic acid residues), and with carrageenans (polysaccharides containing 3-substituted residues of β-D-galactose and 4-substituted residues of α-D-galactose or 3,6-anhydro-α-D-galactose sulfated at different OH groups). Studies on this type of compounds have been stimulated by the fact that they form stable gels in the presence of *s*-metal salts.[77]



4a: R^1 = H, R^2 = OH;
4b: R^1 = OH, R^2 = H

5



6

Study of the complex formation with metals in these polyelectrolytes is complicated by the presence of two types of binding: territorial (non-specific) binding involving hydrated counter-ions, and site (specific) binding involving non-hydrated counter-ions.[78] The latter type of binding corresponds apparently to the formation of a complex with a metal cation on the polyanion surface. At a definite concentration of counter-ions, a stereoregular anionic polysaccharide, for example, carrageenan, acquires a helical conformation.[77,79] In the case of gel formation, *s*-metal cations are coordinated between the chains; this yields domains consisting of double or even triple helices.[79] Some researchers suggest that only single helices participate in intermolecular complex formation.[80] However, it is generally believed that cross-linking of two adjacent chains according to the 'egg box' pattern (Fig. 1*a*) is the primary process.

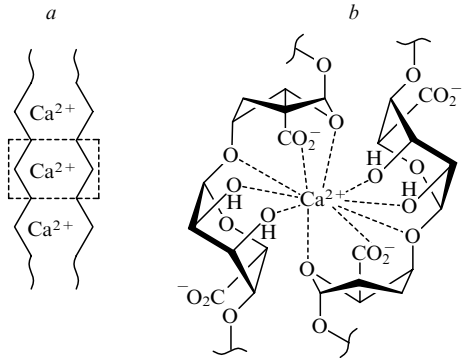
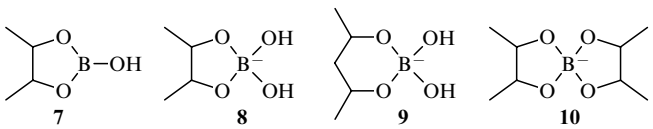


Figure 1. Formation of the intermolecular complex of a polysaccharide with calcium ions.

This model was proposed to interpret the gel formation by poly-L-guluronate in the presence of Ca^{2+} ions.[81,82] Later it was confirmed for systems comprising Ca^{2+} and polygalacturonate **5**[83,84] or Na^+ and alginate **6**.[85] Intramolecular complexation occurs upon the formation of a hydrophilic cavity between monomeric units of neighbouring chains (Fig. 1*b*).[86,87] The formation of these cavities can account for the more efficient binding of Ca^{2+} cations by poly-L-guluronate **5**[87,88] and also for the preferred binding of K^+ and Rb^+ cations by carrageenans.[89,90]

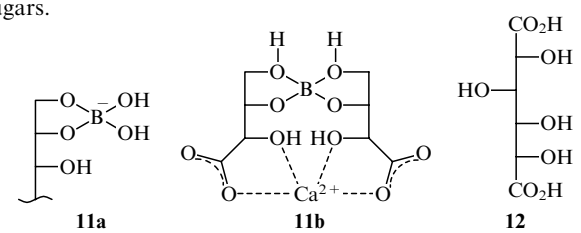
2. Complexes with *p*-metal cations

Borate complexes of carbohydrates are the most studied compounds in this series. They constituted the subject of early classical studies of Böeseken[3] carried out by measuring the electrical conductivity of solutions. Later, the results of this study were supplemented by the data of ^1H (Ref. 91), ^{13}C (Ref. 92), and ^{11}B (Refs 93–95) NMR spectroscopy. This resulted in the detection of neutral complexes **7** (which predominate in acidic media),[92,94] anionic monomeric complexes with five- (**8**)[94] and six-membered (**9**)[94,95] rings, and anionic dimeric complexes **10**[94] of boric acid with polyhydroxyl compounds.



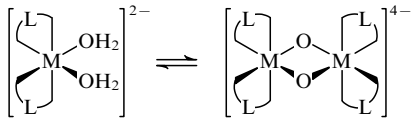
All these products are complexes formed by vicinal hydroxyl groups; nevertheless, complexes of the type **1b** are the most stable in conformity with the second Angyal rule.[91,92,95,96] High stability constants (10^3–10^6 litre mol^{-1})[97–99] imply a covalent character of these complexes; however, they have not been isolated in the crystalline state. Calorimetric,[100] titrimetric,[101] and polarimetric[102] studies have not provided evidence for the existence of the complexes of type **10**. However, they were detected in ^{11}B NMR studies.[94,95]

Borate complexes of acyclic polyols of type **11a** can be additionally stabilised owing to the formation of intramolecular hydrogen bonds. This accounts[103] for the higher stability of these complexes compared to the complexes formed by cyclic forms of sugars.



In aqueous solutions in the presence of borate ions, aldonic and aldaric acids[2] tend to form complexes with Ca^{2+} ions of the composition $CaBL_2$ (L is the ligand). This synergism, which is relatively uncommon in the coordination chemistry of carbohydrates, has been explained[104] by assuming that the preliminary binding of borate ions makes carboxyl groups approach each other, which facilitates the formation of complexes **11b**.

The complexation of sugars with other Group IIIA cations has not received much study. Neutral non-hydrolysable complexes of Ga^{III} with monosaccharide carboxylic acids such as D-glucaric acid (LH_6, **12**) of variable composition have been synthesised.[105] Complexes of In^{III} with D-glucaric acid **12** of the type $[InLH_{-2}]^+$, $[InLH_{-3}]^0$, and $[InLH_{-4}]^-$ were detected (the negative numerals in the subscripts denote the number of substituted hydrogen atoms).[106] The results of a study of complexation of the acid **12** with Al^{III} and Ga^{III} ions carried out by electrophoresis have been interpreted[107] in terms of an equilibrium between monomer **13a** and dimer **13b**, only carboxyl groups of the ligands being involved in the coordination.

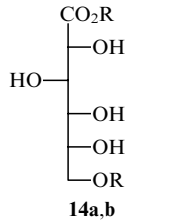


M = Al, Ga.

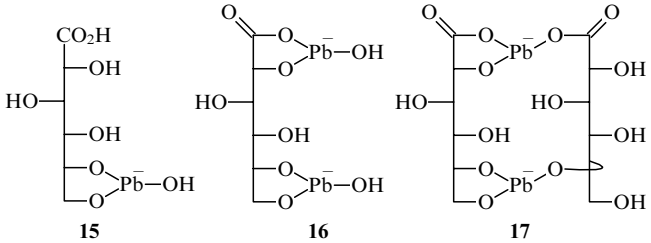
The complex formation of sugars with Group IVA cations is also little studied. It has been noted[108,109] that germanic acid forms complexes of the composition $[Ge(LH_{-2})_2OH]^-$ and $[Ge(LH_{-3})_2]^{2-}$ with acyclic polyols and with α,β-D-glucopyranose **4a**,**b** and also 1 : 1 complexes with pentoses.[98] Note that in the latter case, the first Angyal rule holds. One publication[110] describes the formation of 1 : 1 complexes of aldoses and ketoses with hexahydrostannate at high pH values.

The complexation of sugars with Pb^{II} has been studied somewhat more comprehensively. It has been shown[111] that pentoses and their glycosides form complexes of the composition PbL and PbL_2. However, other researchers[112] claim that only the former type of complexes exists.

D-Xylaric acid reacts with Pb^{II} in an acidic medium to give the complex $PbLH_{-2}$ as a result of deprotonation of the carboxyl groups.[113] In alkaline media, this complex is hydrolysed giving a hydroxo complex.[113] D-Gluconic acid **14a** in an acidic medium binds Pb^{II} only as a monodentate ligand by the carboxyl group; this gives the complexes $[PbLH_{-1}]^+$ and $[Pb(LH_{-1})_2]$.[114] In an alkaline medium, $[Pb(OH)_3]^-$ reacts with D-gluconic acid **14a** to afford complexes **15**–**17**.[115] In solid lead D-gluconate, the metal coordinates two monodentate gluconate residues through the carboxyl groups and two bidentate gluconate residues through the carboxyl group and the hydroxyl group at C(2) (α-type coordination[69]).[116] Thus, the Pb^{2+} cation is surrounded by six oxygen atoms. Evidently, aldaric acids bind Pb^{II} more strongly than aldonic acids.[117]



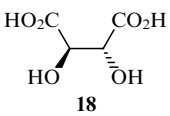
14a: R = H (LH_6);
14b: R = $COCH_2NMe_2$ (LH_5)



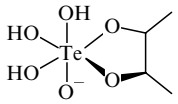
It has been noted [118, 119] that Pb^{II} complexes with oligomeric fragments of the pectate **5** are covalent compounds. In all probability, they contain two carboxyl groups per one Pb^{2+} cation; apparently, this accounts for the high selectivity of formation of Pb^{II} complexes with pectin.[120] The formation of Pb^{II} complexes with pectin can also occur with incorporation between polymer chains.[121]

The complexation of sugars with Group VA elements is little studied. The formation of complexes of monosaccharides and polyols with As^{III} and As^{V} of the composition $[As^{V}(LH_{-2})_3]^-$, $[As^{III}(LH_{-2})(OH)_2]^-$, and $[HAs^{III}(LH_{-2})(OH)_2]$ has been reported.[109, 122] Recently the Bi^{III} complex with L-tartaric acid **18** has been studied by X-ray diffraction analysis.[123] The composition of this complex was found to be $Bi[O_2C(CHOH)_2CO_2][O_2C(CHOH)_2CO_2H]\cdot 3H_2O$. In this complex, two dicarboxylate ligands are coordinated by the carboxyl and α-hydroxyl groups (α-type coordination [69]) and one monocarboxylate ligand is coordinated by the two oxygen atoms of the carboxylate ion. The coordination number of Bi^{III} is equal to nine due to the additional coordination of three water molecules.

Complexes of monosaccharides with telluric acid (Te^{VI}) provide an example of complexes obtained for Group VIA elements. For these compounds, structure **19** was proposed.[124, 125] It was found [126] that in addition to the 1 : 1 complex, saccharose forms the complex $L(TeO_4)_4$.

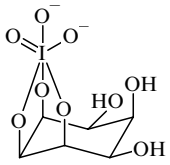


18



19

Complex formation with Group VIIA elements has been studied only for iodine. Apparently, this is due to the fact that periodate oxidation is an important process in the chemistry of carbohydrates.[2] It was suggested [2] that this process starts with the formation of an unstable complex of the IO_4^- anion with a vicinal diol group; the structure of this complex is similar to that of the tellurate complex **19**, because the sizes of the corresponding ions are close. However, monosaccharides conforming to the first Angyal rule should form [127] stable complexes with periodate, for example, a complex of type **20**.



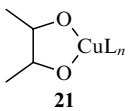
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Later, both the fact of formation of the intermediate complexes and the observance of the first Angyal rule have been confirmed by NMR spectroscopy [127] and paper electrophoresis.[128]

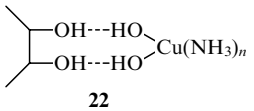
3. Complexes with *d*- and *f*-metal cations

This field of coordination chemistry of carbohydrates has been studied in the greatest detail, although quite irregularly. The vast majority of the data refer to complexes of carbohydrates with Cu, Fe, Co, Ni, Mo, and W.

Among complexes with Group IB metal cations, those with Cu^{2+} have received most study. The dissolution of freshly prepared copper hydroxide in ammonia-containing or alkaline aqueous solutions of polyhydroxyl compounds, including carbohydrates, which has long been used in analytical chemistry, was interpreted [129] as the formation of five-membered diolate complexes **21**. The stability constants of these complexes for L = NH_3 are of the order of 10^2-10^4 litre mol^{-1}. In thiscase,complexes of the 1 : 1 composition are always formed.[129–131] The assumption [132–134] that cuprammonium complexes of vicinal diols are formed as structure **22** (which apparently involves hydrogen bonds) is hardly consistent with both the stability of these complexes and the maintenance of fixed dihedral angles between the coordinated oxygen atoms.[6]



21

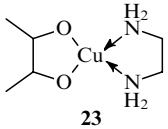


22

L = NH_3, H_2O, OH^-.

The structure **22** also does not agree with the observed induction of optical activity in the central atom (the appearance of optical activity in its electronic transitions);[135] in fact, in the complex **22**, this would be less likely than in the complexes **21**, because in the former case, the chiral centres (inducers) are further removed from the central atom.

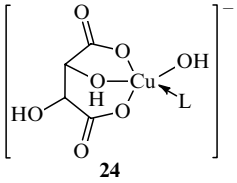
Mannitol was found to form the complex $[Cu(LH_{-2})]$ when the ligand is present in a large excess [136] or Cu_2L when the reactants are present in equimolar amounts.[136] The latter complex is apparently anionic. This was confirmed [137] by isolation of a series of analogous anionic copper complexes of carbohydrates. An isomer of mannitol, sorbitol, forms the complex $[Cu_3(LH_{-6})]$ in strongly alkaline media [138] and a polymeric complex in less alkaline media. An NMR study with the use of a shift reagent has confirmed [139] that Cu^{II} is mostly coordinated to vicinal diol groups of the ligand, although the first Angyal rule can also be observed.[140] In neutral and acidic media, polyols do not coordinate Cu^{II} ions.[141] This would require [130] deprotonation of at least one hydroxyl group. Structure **23** similar to **21** was ascribed [142] to complexes containing ethylenediamine in place of ammonia.



23

The complexation of Cu^{II} with carbohydrate carboxylic acids has also been studied fairly comprehensively, although, as in the previous cases, these complexes have not been isolated in the solid state. D-Galacturonic acid forms [143] the complexes $[CuL_2]^{2+}$, $[CuL_2H_{-1}]^+$, $[Cu(LH_{-1})_2]$, and $[CuL_2H_{-4}]^{2-}$, whereas D-glucuronic acid forms only the second type of complex.[143] In this case, coordination involves the ring oxygen atom,[144] as has also been observed for *s*-metal cations (Section II.1). D-Gluconic acid **14a** or its dimethylglycine ester (**14b**, pangamic acid, vitamin B_{15}) form mixed-ligand copper complexes in the presence of glycine;[145] the structure of these complexes is unknown.

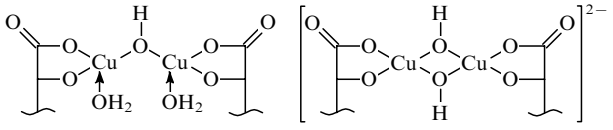
Glucaric acids form complexes with Cu^{II} according to the α-type of coordination (Section II.1). The tartaric acids **18** give hydroxo complexes **24** [146, 147] containing a water, ammonia, or amine molecule as a ligand. In the case of D-glucaric acid **12**, formation of the complexes $[Cu(LH_{-3})]^-$ (at pH 3.65) and $[Cu(LH_{-2})_2]^{2-}$ (at pH 5–9, coordination only through the carboxyl groups) and formation of the polymer $[Cu(LH_{-3})_n]^{n-}$ (coordination through the carboxyl group of one ligand and the α-type coordination in another ligand) have been reported.[148]



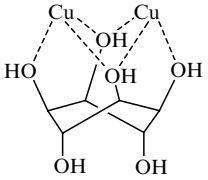
24

L = H_2O, NH_3, RNH_2.

Binuclear copper complexes of sugars are less frequently encountered. For example, D-gluconic acid **14a** can form [7, 149] complexes of type **25a** or **25b**. In addition, one of the bridging hydroxyl groups in the complex **25b** can be deprotonated. At a favourable arrangement of four vicinal hydroxyl groups (which occurs, for example, in mucoinositol), sugars in cyclic and acyclic forms can react with Cu^{II} at pH 5 yielding binuclear complexes of type **26** in which the hydroxyl groups of the tetradentate ligand occupy bridging positions.[150]



25a **25b**



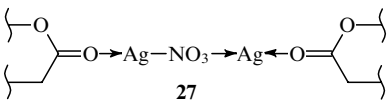
26

Considerable attention has been devoted to the study of complexation of Cu^{II} with polysaccharides. Thus dissolution of cellulose in a cuprammonium solution is an important technological process, which has been studied most vigorously.[151] The formation of chelates of the type **21** with coordination through the hydroxyl groups at the C(2) and C(3) atoms of β-D-glucopyranose **4b** is considered to be the most likely. Polymers having a similar structure, dextrans, are also capable of binding Cu^{II} cations in alkaline media.[152, 153] This process might be accompanied by untwisting of the helical chains of the ligand.[152] The formation of complexes of the type **23** is apparently responsible for the adsorption of the complex $[Cu(en)_2]^{2+}$ (where en is ethylenediamine) on cellulose fibres.[154]

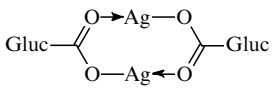
Study of complexation of Cu^{II} with anionic polysaccharides has shown [155] that D-galacturonate itself binds Cu^{II} more strongly than its polymer, polygalacturonate **5**. The affinity for Cu^{II} decreases in the following sequence: pectate (polygalacturonate) **5** > alginate **6** > polymannuronate. A similar situation was observed for Ca^{II} ions.[156] The complex formation is a cooperative process.[156, 157] The ligand unit in the copper complexes of pectic acids has [158] an octahedral configuration, the Cu^{II} cation being coordinated to four oxygen atoms in the symmetry plane.

The formation of Cu^{II} complexes with anionic polysaccharides changes substantially the conformation of the polymer chains of the ligands. As in the case of Ca^{II}, the complex formation is a cooperative process.[156, 157] As this takes place, a sulfated polysaccharide, ι-carraginane, passes into a helical conformation.[159]

The formation of complexes of carbohydrates with Ag^{I} has been studied only for the silver nitrate – D-glucurono-δ-lactone [160] and silver nitrate – D-glucurono-γ-lactone [161] systems. It was concluded that in both cases, this affords two types of complexes: 'lactone' complex **27** and 'carboxyl' complex **28**.

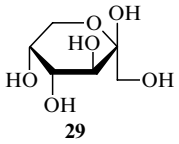


27

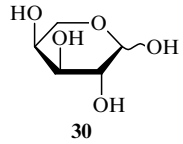


28

Among complexes with cations of Group IIB *d*-metals, compounds of Zn^{II} and Cd^{II} have been studied most thoroughly. β-D-Fructopyranose **29** and L-arabinopyranose **30** react with these cations, as with Hg^{II} cations, to give solid complexes of the composition $[MLX_2 \cdot 4H_2O]$, where X = Cl, Br. In the complex of fructose, the coordination involves two ligand molecules; one of them binds the central ion through the O(2) and O(3) atoms and the other one binds this ion through O(4) and O(5).[162] In the case of L-arabinopyranose **30**, the two ligands are also coordinated through different sites: the O(3) and O(4) atoms of one molecule and the O(1) and O(5) atoms of the other molecule.[163]



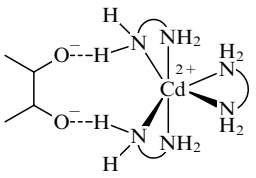
29



30

In the Zn^{II} and Cd^{II} complexes with both ligands (**29** and **30**), the metal ion coordinates additionally two water molecules, and thus its coordination number is equal to six. For the Hg^{II} cation, there is no coordination with water (the coordination number is four). The counter-ion of the initial salt is bound to the metal cation by electrostatic forces.

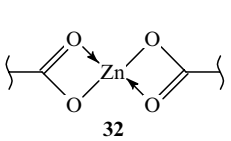
Sugars and their *O*-glycosides react with cadoxen (a solution of cadmium hydroxide in ethylenediamine) to give complexes incorporating two deprotonated equatorial hydroxyl groups of the pyranose ring. Presumably, they have the structure **31**.[164]



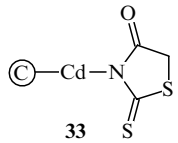
31

This structure is additionally stabilised by hydrogen bonds. However, as in the copper complexes **22**, in this case, too, it is difficult to explain the observed induction of optical activity in the electronic transitions of Cd^{II}.[165]

D-Gluconic acid **14a** and Cd^{II} form complexes with a Cd : L ratio of 1 : 2 (pH 5.8), 2 : 3, and 2 : 1 (pH 13 – 14).[166] D-Glucuronic acid forms two types of solid complexes with Zn^{II}, Cd^{II}, and Hg^{II}: complexes produced *via* coordination through the carboxyl group and the ring oxygen atom of the first ligand molecule and the carboxyl group and the O(4) atom of the second molecule and those (**32**) in which coordination involves only the carboxyl groups.[167] In the *O*-methylglycoside of D-glucuronic acid, Zn^{II} is bound to the carboxyl group and to the ring oxygen atom.[16] It has been noted [148] that D-glucaric acid **12** forms a complex with Cd^{II}, but its structure has not been described.



32



33

Ⓒ is a cellulose fragment.

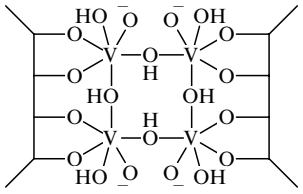
Complex formation of *O*-methylglucosides in aqueous solutions of zinc chloride has been reported.[168] Presumably, the metal ion is coordinated to the O(2) and O(3) atoms. The complex formation accounts [168] for swelling of cellulose in these solutions.[151] Cellulose is known [151] to dissolve in cadoxen. Apparently, this yields polymeric complexes like **31**. The reaction of rhodanine with cellulose in the presence of a cadmium salt gives rise to complex **33** with different ligands.[169] Substituted rhodanines afford similar complexes.[170]

It was found that cadmium(II) [171] and zinc(II) [172] ions are bound to pectate **5** through the carboxyl groups, although the α-type coordination also cannot be ruled out. A similar situation is observed in the case of oligosaccharide fragments of pectic acids.[172]

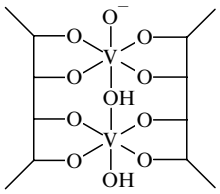
Complexes of carbohydrates with Group IIIB *d*-metals are represented by Y^{III} complexes of tartaric acid, the composition of which varies from 1 : 1 to 1 : 5 depending on the pH,[173] and by Y^{III} complexes of D-gluconic acid **14a**, the composition of which is 1 : 1 and the charge varies depending on the pH.[174, 175] Complexes of La^{III} with tartaric, D-glucaric **12**, and D-galactaric acids have been obtained, their composition (1 : 1 or 1 : 2) being also dependent on the pH value.[176] No data on the structures of these complexes have been reported.

Several complexes formed by Group IVB elements are known. These are Ti^{IV} complexes[177] with tartaric (**18**) and D-gluconic (**14a**) acids and with mannitol (their composition is 1 : 1 or 1 : 2 depending on the pH), the Zr^{IV} complex with trihydroxyglutaric acid $[Zr(OH)_3(LH_{-2})]^-$,[178] and Zr^{IV} and Hf^{IV} complexes with tartaric, trihydroxyglutaric, and D-galactaric acids, which have similar structures.[179]

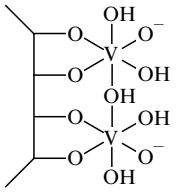
The known complexes of Group VB *d*-metals are mostly formed by vanadium. For example, metavanadate in aqueous solutions reacts with aldoses to give complexes incorporating the $[VO_3L]^-$ and $[(VO_3)_2L]^{2-}$ anions.[180] In the latter case, complex formation is observed only for D-glucitol (sorbitol) and maltose (which is a disaccharide). L-Tartaric acid **18**, its D-enantiomer, and the corresponding racemate form binuclear complexes with the vanadyl ion VO^{2+}; the composition of the complexes is $[(VO)_2L_2H_{-n}]^{(n-4)-}$ (n = 5, 6, or 8 depending on the pH).[181] Mesotartaric acid forms a trinuclear complex, $[(VO)_3L_3H_{-8}]^{2-}$. For polynuclear complexes of acyclic polyols and aldonic acids in aqueous solutions, several types of structures containing tetradentate ligands have been proposed (structures **34**–**36**).[181, 182]



34



35

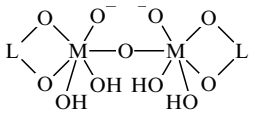


36

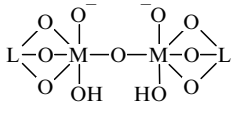
Cyclic sugars and vanadate ions form mononuclear cyclic esters of 1 : 1 composition.[183] In the most stable complexes characterised by the *cis*–*cis* arrangement of three vicinal hydroxyl groups (for example, in the complex of β-D-mannopyranose), the ligand is coordinated in a tridentate manner, while in the other cases, in a bidentate manner. Polygalacturonates **5** are coordinated to $V^{IV}O$ ions through the carboxyl groups.[184] At pH 3–7, Nb^V ions and D-gluconic acid form the complexes $[Nb(OH)_n(LH_{-2})]^{(4-n)-}$, while at pH 7–9, the complexes $[Nb(OH)_m(LH_{-2})]^{(3-m)-}$ are produced.[185]

The complexation of sugars with cations of Group VIB *d*-metals has been studied fairly intensively. Primary attention has been devoted to complexes of molybdenum and tungsten. Chromium(III) cations do not form stable complexes with sugars in aqueous solutions,[186] whereas in dry methanol, aldoses form complexes with $CrCl_3 \cdot Py$ (Py is pyridine); the composition of these complexes is 1 : 3 (aldose : $CrCl_3 \cdot Py$).[186] Conversely, D-glucaric acid **12** (and, perhaps, all the aldaric acids) and Cr^{III} in aqueous solutions form an equilibrium system, similar to the **13a** ⇆ **13b** system.[107] It has also been reported[187] that a stable complex of Cr^V of an unknown structure is formed during oxidation of D-galacturonic acid with Cr^{VI} cations.

The complex formation of sugars and Mo^{VI} and W^{VI} oxo cations has been studied most comprehensively. Since the structures of carbohydrate complexes formed by these metals are similar,[188–190] they will be discussed together. In most cases, binuclear complexes ML_2 with bidentate (complex **37**) and tridentate (complex **38**) types of ligand coordination are produced in aqueous solutions. The structure of **37** was unambiguously established only for the molybdenum complex of D-glucuronic acid *O*-methylglycoside. According to X-ray diffraction analysis,[15] this complex is characterised by the α-type coordination. For carbohydrates existing in acyclic forms (alditols, aldonic acids), this type of coordination is accomplished in one tetradentate ligand in which the neighbouring hydroxyl groups occupy *cis*-positions.[191–194] The complexes like **38** are formed in conformity with the first Angyal rule[193, 194] even if the initial chair-like conformation of the pyranose ligand is distorted.[195, 196]



37

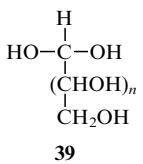


38

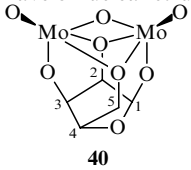
M = Mo, W.

Since, due to their conformational mobility, acyclic forms of sugars are more prone to form complexes, it has been assumed and, to some extent, confirmed[197] that the hydrate of the aldehydo form **39** participates in the complex formation. It has been reported[198] that D-lyxose, D-mannose, and L-rhamnose are coordinated as tetradentate ligands only in the cyclic pyranose form, although D-lyxose in the furanose form can be also coordinated in this way (see structures **40** and **41**). However, other researchers[199] claim that these ligands are coordinated in a tridentate fashion. Upon the interaction of W^{VI} ions with an acyclic polyol (sorbitol), in addition to the tetradentate coordination (1 : 1 complexes as two regioisomers), a complex of the type **37** in which the ligand is coordinated bidentately has been detected.[200] The carbohydrate complexes of W^{VI} are three orders of magnitude more stable than complexes of Mo^{VI}. This is due[198] to the fact that W^{VI} forms polyoxo anions more readily than Mo^{VI}.

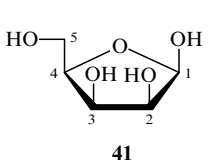
Attempts to determine the structure of the carbohydrate complexes of Mo^{VI} and W^{VI} by X-ray diffraction analysis are not always successful. Thus, according to X-ray diffraction data,[201] the crystalline compound isolated upon the interaction of D-xylofuranose with ammonium molybdate proved unexpectedly to be a complex of D-lyxose **40**. The transformation of D-xylose into D-lyxose, which is the C(2) epimer of the initial ligand, was explained by the Lobry de Bruyn–Alberda van Ekenstein rearrangement occurring during the synthesis of the complex (Section VI.2). It was shown that the new ligand is coordinated in the furanose form **41**. Later, using X-ray diffraction analysis, a similar structure has been found for the molybdenum complex of an acyclic tetraol (erythritol).[202] Based on ^{13}C and ^{95}Mo NMR spectra, it was shown that in solutions, molybdenum complexes of other acyclic polyols (mannitol, *etc.*) have similar structures.[203] After these publications, there are grounds for believing that the other Mo^{VI} and W^{VI} oxo complexes discussed above also have binuclear structures of the type **40**.



39



40



41

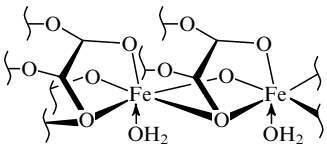
n = 1–4.

Among complexes of carbohydrates with Group VIIB *d*-metals, complexes of manganese in various (including low) oxidation states have been studied in most detail, because the low oxidation states of manganese, which are generally unstable,

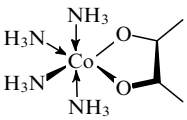
can be stabilised by acyclic polyhydroxyl ligands in aqueous solutions.[204] The greater the number of hydroxyl groups in the ligand, the more pronounced this stabilisation, because, according to the principle of hard and soft acids and bases,[205] the Mn cations are more firmly bound to hydroxyl groups than to carboxyl groups.[204] Judging by the results of electron–nuclear relaxation measurements, carbohydrates in the pyranose form coordinate only weakly Mn^{II} ions by the O(3), O(4), and O(6) atoms [206] (see the structures **4a**,**b**). It should be noted that acyclic polyols also weakly coordinate Mn^{II}, but they form stable complexes with Mn^{III} and Mn^{IV}ions.[204] However, it was stated [207] that the complexes of sorbitol with Mn^{II} ions are also stable. The composition of complexes of acyclic polyols with Mn^{III} was found [204,207] to be 1:2 or 1:3. In aqueous solutions, D-gluconic acid **14a** forms complexes $[Mn^{II}(LH_{-2})_2]^{2-}$, $[Mn^{III}(LH_{-2})_2OH]^{2-}$, and $[Mn^{IV}(LH_{-2})_3OH]^{3-}$ (from data on electrochemical oxidation with variation of the electrode potential).[208] The former complex is able to dimerise with successive deprotonation yielding a series of binuclear compounds. The complex of D-gluconic acid of the composition $[Mn^{IV}(LH_{-2})_3OH]^{3-}$ is the first example of a stable carbohydrate derivative of Mn^{IV}. In the solid Mn^{II} gluconate, which is the only carbohydrate complex of manganese studied by X-ray diffraction analysis,[209] the central ion was found to have an octahedral environment formed by two ligands and containing the carboxyl and hydroxyl oxygen atoms. These ligands exist in two conformations: a zigzag-like (similar to that of alkanes) and a bent conformation. The same conformation of the carbohydrate ligand was found in an aqueous solution of Mn^{II} gluconate.[210] Tartaric acid **18** forms a neutral Mn^{II} tartrate,[211] which is deprotonated upon an increase in the pH, and in alkaline solution, it is oxidised by atmospheric oxygen to give hydroxytartrate complexes of Mn^{III}.[212] Manganese(II) does not form complexes with D-glucaric acid **12**.[148] It has also been noted that Mn^{II} is bound by dextrans [153] and by polygalacturonate **5**.[184]

Rhenium(VII) as perrhenate forms complexes with alditols (acyclic polyols), aldonic acids of the type **14a**, and their lactones. The complexation involves two hydroxyl groups having the *R*- and *S*-configuration, respectively.[213] It is believed that pertechnetates form no complexes with these ligands.[213] However these data are disproved in another publication.[214]

Among Group VIII elements, metals of the iron subgroup are represented most widely in the coordination chemistry of carbohydrates. Thus sugars and other polyhydroxyl compounds form stable complexes with Fe^{III} ions.[215] D-Glucopyranose **4a**,**b** [216] and D-fructopyranose **29** [216–218] are the best complexones. Structural studies on the Fe^{III} complex of D-fructopyranose **29** confirm the polymeric polynuclear structure **42**.[216] In an aqueous solution, the polymer **42** occurs in equilibrium with monomeric and dimeric complexes.



42



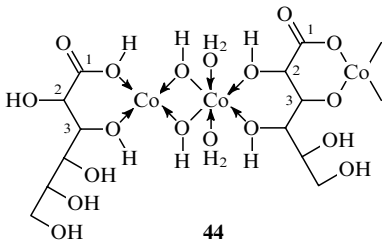
43

The complexation of Fe^{III} with tartaric acid **18** in an alkaline medium leads to the complex $[Fe(LH_{-3})_3]^{6-}$ with coordination through both carboxyl groups and a hydroxyl group.[219] Apparently, a complex of the type **24** is formed. A ternary complex of the composition 1:1:1 was isolated from the Fe^{III}–sodium tartrate–saccharose system.[220] This accounts for the dissolution of cellulose in iron–tartrate solutions.[151] The following heteronuclear iron–vanadium tartrate complexes were prepared:[221] $[FeVO(LH_{-2})_2]^{+}$, $[FeVO(LH_{-3})(LH_{-4})]^{2-}$, and $[FeVO(LH_{-4})_2OH]^{4-}$.

D-Gluconic acid **14a** forms [7,222] chelates with Fe^{III} with bi- and tridentate coordination through only hydroxyl groups. Later,[223] similar structures have been proposed for Fe^{III} complexes with trihydroxyglutaric acid. However, in this case, coordination can involve either one [223] or two [148] carboxyl groups. The complexes of this type are fairly stable ($K_s = 10^4–10^5$ litre mol^{-1}).[224,225] Preparation of polymeric Fe^{III} complexes of the type **42** with sorbitol or D-glucuronic acid has been reported.[226]

Cobalt(II) and nickel(II) cations form 1:1 coordination compounds with mannitol.[136] Ammonia complexes of Co^{III} react with D-ribose and L-sorbose to give chelates $[Co(NH_3)_4L_2]^{3+}$ chiroptical properties of which point to a structure like **43**.[227] In addition to these chelates, Co^{II} ions form a binuclear complex $[Co_2(NH_3)_3(OH)_2(H_2O)_2L]^{3+}$ with D-arabinose.[228]

In the series of carbohydrate carboxylic acids, complex formation of Co^{II} and Ni^{II} with D-gluconic acid **14a** has been studied most extensively. It has been noted [4] that this is not accompanied by substantial changes in the ligand conformation and that Ni^{II} chelates are more stable than Co^{II} chelates.[229] It was found that in an acidic medium, unstable complexes $[M(LH_{-1})]^{+}$ are formed.[230–232] Polynuclear complexes $[Co_2(OH)_3(LH_{-1})]\cdot H_2O$ and $[Co_3(OH)_2(LH_{-2})_2]\cdot 2H_2O$ were detected in the pH range of 7.5–9.5.[231] The latter is a polymer of structure **44**. The complexes $[Ni_2(OH)_3(LH_{-1})]$ and $[Ni_2(OH)_4(LH_{-1})]^{-}$, which might have a similar structure, have been obtained.[230] Tetraamminecobalt(II) reacts with D-gluconic (**14a**) and D-glucuronic acids to give the complexes $[Co(NH_3)_nL]^{2+}$ ($n = 4, 5$) in which the ligands behave as monodentate ones.[233] Study of solid nickel gluconates $[Ni(LH_{-1})_2]\cdot 2H_2O$ and $[Ni_2(OH)_2(LH_{-2})]\cdot 2H_2O$ by spectroscopic and magnetic methods has shown that the chelate units in both complexes have a distorted octahedral configuration.[234] The second complex has a polymeric structure with hydroxyl bridges, apparently, similar to the structure **44**.

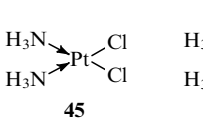


44

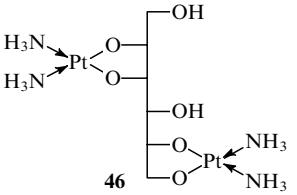
The diastereomeric Λ- and Δ-complexes $[Co(LH_{-1})(en)_2]^{+}$ have been obtained by the reaction of racemic $[Co(CO)_3(en)_2]^{2+}$ with aldonates and separated.[13] Aldaric acids form [148] chelates of the type $[M(LH_{-3})]^{-}$, the structure of which is apparently **24**, and a binary complex $\{[Ni(bipy)_3]_2(LH_{-2})\}$ (bipy is bipyridine).[235]

Data on the complexation of Co^{II} and Ni^{II} with polysaccharides are scarce. Thus it is known that these cations are bound by dextrans [153] and polygalacturonate **5** [184] and that cellulose dissolves in solutions of the complexes $[Co(en)_3(OH)_2]$, $[Ni(NH_3)_6(OH)_2]$, and $[Ni(en)_3(OH)_2]$ yielding complexes of an unknown structure [151] (supposedly of the type **31**).

Complexation of carbohydrates with cations of platinum group metals has been studied mostly in connection with their therapeutic effect (Section VI.1). When cisplatin **45** was made to react with D-mannitol, two complexes with identical structures (**46**) but with different colours and different chiroptical properties were isolated.[236] The reasons for this result are unknown.

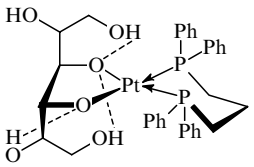


45

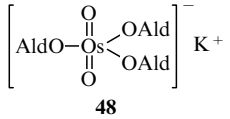


46

The reactions of acyclic polyols with the 1,3-bis(diphenylphosphino)propane platinum complex result in the formation of stable diolate chelate-type complexes **47**, which are additionally stabilised by intramolecular hydrogen bonds.[237] The complexes have been structurally characterised. The reaction is regioselective and occurs most efficiently with vicinal diol groups. Peculiar anionic complexes, so called osmarines, are formed upon the reaction of osmium salt **48** with aldoses.[238, 239]



47



48

Ald is the aldose residue.

These complexes are polymers the backbone of which consists of linked (possibly, *via* oxygen) Os atoms with 'grafted' monosaccharide residues. The molecular masses of these compounds are between 10^3 and 10^6 dalton. Some of the aldose fragments are oxidised to aldonic acids during complex formation; therefore, the complexes can be described by the general formula $K_mOsO_nY_xZ_y(H_2O)_z$, where Y is aldose, Z is aldonate (the therapeutic properties of these polymers are described in Section VI.5).

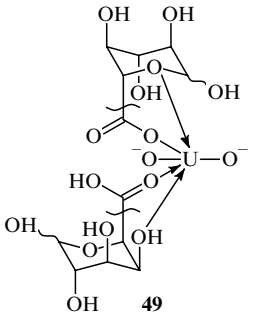
D-Gluconic acid **14a** forms two extremely stable complexes of the composition 1 : 1 with Pt^{II} cations; these products result from slow hydrolysis of the initial polymers of the composition 6 : 1.[7] The Ru^{III} cation also forms a stable complex compound with D-gluconic acid in an alkaline medium.[240] Similar stable complexes of D-gluconic acid have been obtained for Os^{III}, Os^{IV}, and Os^{VI} ions.[241] Mixed-ligand chelates [PtL(1,3-diamine)] have been obtained with D-gluconate and D-glucuronate in the presence of 1,3-diamines.[242]

Among the complexes formed from *f*-metals with sugars, those of lanthanides have been studied most thoroughly. The use of water-soluble lanthanide salts as shift reagents in NMR spectroscopy has demonstrated that the first Angyal rule holds for both cyclic[243] and acyclic[244] carbohydrate forms, while the second Angyal rule is obeyed for furanoses,[245] *i.e.* there is a similarity between the behaviours of lanthanides and *s*-metals.

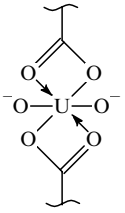
The complexation of lanthanide cations with carbohydrate carboxylic acids has been studied fairly comprehensively. The chiroptical properties of the complexes of lanthanides with tartaric acid **18** are discussed in a review.[246] The α-type bidentate coordination and tridentate coordination through both hydroxyl groups and the carboxyl group have been assumed for the complexes resulting from the reaction of glyceric acid with Co^{III}.[247] D-Galacturonic acid coordinates Eu^{III} ions through the oxygen atom of the carboxyl group, the hydroxyl group at the C(4) atom, and the ring oxygen atom (1 : 1 complex),[248] while the *O*-methylglycoside of this acid binds Eu^{III} only by the carboxyl group and the ring oxygen atom {the $[Eu(LH_{-1})_3]$ complex}.[249]

D-Gluconic acid **14a** forms the most stable chelates with Ce^{III} ions.[4] Structures with the α-type coordination and with tridentate coordination involving the carboxyl group have been proposed for 1 : 1 complexes of lanthanides.[250, 251] The stability constants of these complexes at low[252] and high[253, 254] pH values have been determined. An increase in the gluconate concentration leads to the formation of complexes $[M(LH_{-1})_n]^{(3-n)+}$, where $n = 2-4$.[255]

As regards actinides, only data on the complex formation of U^{VI} (as the uranyl cation, UO_2^{2+}) have been reported. This cation coordinates aldopyranoses and cyclic polyols at pH > 10 without observance of the first Angyal rule. Apparently, this is due to its large size.[199] D-Glucuronic acid forms complexes **49** and **50** with these ions.[259] Similar complexes are produced in the case of tartaric acid **18** and trihydroxyglutaric acid.[257]



49



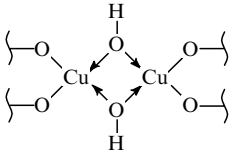
50

III. Complexes of cyclodextrins

Cyclodextrins (CD) are cyclic oligosaccharides consisting of six (α-CD), seven (β-CD), or eight (γ-CD) residues of α-D-glucopyranose **4a**. They are capable of incorporating various organic molecules into inner hydrophobic cavities.[258–262]

Less is known of the ability of cyclodextrins to form complexes with metal ions. Thus β-CD complexes alkali metal salts, although this mostly occurs due to binding of the anion.[263] Complexes of α-CD with iodine of the type $(\alpha\text{-CD})_2 \cdot LiI_3 \cdot I_2 \cdot 8H_2O$ (a model of the blue iodine complex with amylose) and with cadmium ions have been described.[264] In the β-CD complex with KOH, the K^+ ion is bound by six coordinate bonds with the hydroxyl groups of the glucopyranose residues thus forming a distorted trigonal prism.[265] The lutetium ion can also be bound to β-CD.[266] Metal complexes of coronands (crown ethers)[267, 268] or their acyclic analogues, podands,[268] can be incorporated into the cavities of cyclodextrins.

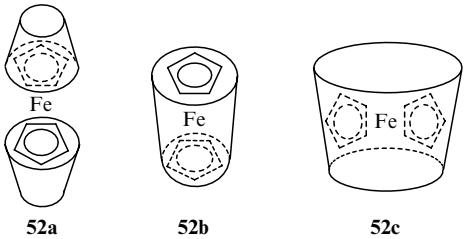
Some complex compounds of cyclodextrins with *d*-metal cations are also known. α-Cyclodextrin forms binuclear complexes **51** with Cu^{II}; complexes of β-CD are formed similarly but contain deprotonated oxygen bridges.[269–271]



51

Other *d*-metals are also prone to form polynuclear complexes with β-CD. For example, the complexes $[M_2(OH)_2(\beta\text{-CD}) \cdot 2H_2O]$ (M = Mn^{III}, Cr^{III}), $Na_2[M_2(OH)_2(\beta\text{-CD}) \cdot 2H_2O]$ (M = Co^{II}, Ni^{II}, Cu^{II}), and $[M_4(OH)_4(\beta\text{-CD}) \cdot 2H_2O]$ (M = Fe^{III}) have been described.[272, 273]

However, the primary attention is paid to the inclusion of *d*-metal complexes into cyclodextrin cavities (second-sphere coordination).[274, 275] Thus α-, β-, and γ-CD form host–guest complexes (inclusion compounds) **52a**, **52b**, and **52c**, respectively, with ferrocene.[276–278]



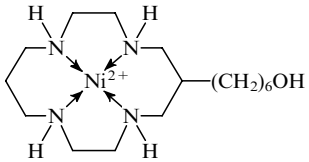
52a **52b** **52c**

The 'guest' molecules in these complexes can rotate freely only at elevated temperatures.[279] The axial incorporation of ferrocene in the complex **52b** was confirmed in a study of complexation of cyclodextrins with a model ferrocene derivative that can be arranged in the cavity only equatorially, as in the complex **52c**.[280] Since the cavity of α-CD is small, it can incorporate only

monosubstituted ferrocenes, whereas the other cyclodextrins form complexes with disubstituted ferrocenes as well.[277,278] In this type of cyclodextrin complex, a chiral 'host' molecule induces optical activity in a 'guest' molecule. This facilitates investigation of these compounds.[281,282] The complex $[(\eta^5\text{-}C_5H_5)FeC_6H_6]PF_6 \cdot 2\alpha\text{-CD}$[283,284] of the type **52a** and its analogues containing naphthalene, indan, tetralin, or thiophene instead of benzene[284] have been prepared. Complexes of η^6-arenetricarbonylchromium with β- and γ-CD of the composition 1 : 1 are known.[285]

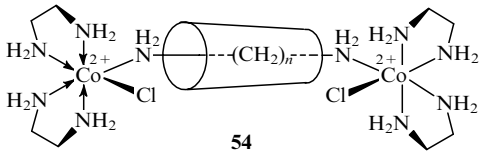
Incorporation of organometallic π-complexes such as $[(\eta^3\text{-allyl})Pd]$,[286] $[(cod)RhCl_2]$ (cod is cyclooctadiene),[287] $[(cod)PtX_2]$ (X = Cl, Br, I),[287] $[(cod)Rh(NH_3)_2]$,[288–290] and ordinary platinum complexes such as **45**[290–293] into cyclodextrins has been studied.

Bulky metal complexes such as macrocyclic Ni^{II} complex **53**[294] or the Fe^{III} complex with protoporphyrin IX (hemin)[295] can also occupy the hydrophobic cavities of cyclodextrins.



53

Rotaxane complexes of type **54** have been synthesised.[296–299] Since the CD molecule is chiral, the synthesis involves asymmetric induction and yields predominantly stereoisomers with the (Δ,Δ)-configuration of the chelate units.[298,299]

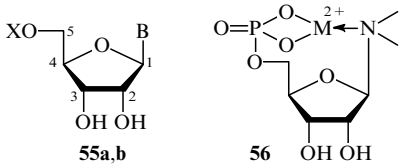


54

n = 8, 10, 12, 14.

IV. Complexes of nitrogen-containing natural carbohydrates

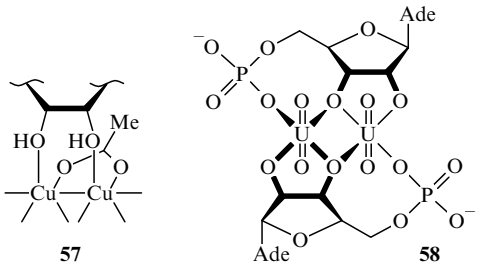
In the metal complexes of ribonucleosides **55a**, metal ions are normally coordinated to endocyclic nitrogen atoms in a base of the pyridine type (B).[300–303] In the case of ribonucleotides **55b**, additional coordination to the phosphate group is possible; this gives cyclic complexes of the type **56**,[18] in conformity with the principle of hard and soft acids and bases.[205]



55a,b **56**

X = H (**a**), PO_3H_2 (**b**); B is a heterocyclic base.

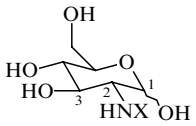
However, within the scope of this review we are interested in the exceptions to this rule, namely, complexes resulting from coordination of carbohydrate fragments. Thus in disodium uridine 3′-phosphate, the Na^+ cation is coordinated not only to the phosphate but also to the oxygen atoms at C(2′) and C(5′).[304] Likewise, the ribose residue is one of the sites of coordination of the Li^+ ion to the nucleosides **55a**.[305] In the sodium inosine phosphate, the Na^+ cation is coordinated to the hydroxyl groups at the C(2′) and C(3′) atoms of the ribose residue.[306] The interaction of borate ions with pyrimidine nucleosides involves coordination at the vicinal diol group at C(2′) and C(3′) and results in a complex of the type **8**.[307] Vanadate ions are coordinated in a similar way.[183,308] The same hydroxyl groups and Cu^{II} ions give binuclear complexes Cu_2L_2 of the type **51**.[309,310] It has been suggested that Cu^{II} acetate forms three-dimensional binuclear complexes like **57**;[311] however, other results[312,313] attest to the formation of ordinary coordination units of the type **21**. The uranyl complex of adenosine has the binuclear bridged structure **58**.[314,315] Desoxyribonucleosides and -nucleotides do not contain a vicinal diol group; therefore, their carbohydrate fragments do not participate in coordination.



57 **58**

Among natural aminosaccharides, D-glucosamine (2-amino-2-desoxy-D-glucopyranose, **59a**) has received most attention. Metal complexes of D-glucosamine have been studied by electronic spectroscopy, potentiometric titration, calorimetry, and EPR spectroscopy. No X-ray diffraction data for these complexes are available.

The complex formation of D-glucosamine **59a** with Cu^{II} has received the most study.[141,316–324] This interaction involves coordination not only to the amino group but also to the hydroxyl groups at the C(1) and C(3) atoms adjacent to the amino group.[316,321] In the complexes CuL and CuL_2,[317,320] the hydroxyl groups of the ligands can be either free[321] or deprotonated.[323] Other researchers[141] deny participation of free hydroxyl groups in the coordination and assume that deprotonation is typical first of all of the hydroxyl group at C(1), because it is the most acidic.[325] In the case of the Cu^{II} complex of *N*-acetylglucosamine **59b**, the *N*-acetyl group is not coordinated to the Cu^{II} ion but stabilises the complex $[Cu(LH_{-1})_2(OH)_2]^{2-}$.[141]



59a: X = H;
59b: X = Ac

59a,b

The complexation of D-glucosamine **59a** with Ni^{II},[141,319–322] Co^{II},[316,319–324,326,327] and Fe^{III} [317–320] ions has been studied fairly comprehensively. For complexes of the composition ML, the following stability series was obtained: $Cu^{II} > Pb^{II} > Zn^{II} > Ni^{II} \equiv Co^{II}, Cd^{II}, Mn^{II} \gg Ca^{II}, Mg^{II}$,[321] and for complexes ML_2, $Fe^{III} > Cu^{II} > Co^{II}$.[319]

The formation of complexes of D-glucosamine **59a** of the composition ML_2 with the above cations is a multi-stage process,[319,323] which includes coordination of the cation to the amino group of the first ligand, to the amino group of the second ligand, coordination to the neighbouring hydroxyl groups followed by their stepwise deprotonation, and finally coordination to a hydroxide ion in a strongly alkaline medium.[323,326] However, other investigators[141,321] deny the possibility of coordination to a hydroxide ion. Solid hygroscopic complexes of D-glucosamine of the composition ML_2 with Ca^{II}, Ba^{II}, and Sr^{II} have been obtained.[324]

The cationic complexes $[FeL(OH)_2]^+$ and $[FeL(OH)]^{2+}$ are formed from Fe^{III} and D-glucosamine **59a** in a physiological salt solution.[326] The crystalline complexes $[NiL_2]X$ (X = 2Cl, SO_4^{2-}) have been obtained.[327] Synthesis of *cis*-dichlorobis(D-glucosamine)platinum(II) has been reported.[328]

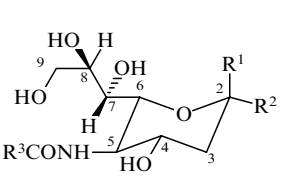
The interaction of D-glucosamine **59a** with tris(ethylenediamine)cobalt has led to contradictory results. First, it was reported[329] that this gives an outer-sphere complex with a structure of the type **31**. Subsequently, it was shown[330] that this affords four isomers with a Δ : Λ ratio of 7 : 3, which differ in the

anomeric configuration of the ligand and configuration of the chelate unit (complexes like **43** with an amino group instead of a hydroxyl group). Finally, recently [331] it was shown that the composition of the product mixture is even more complicated; eight(!) isomers were isolated from the mixture and characterised by X-ray diffraction analysis. In all of these compounds, the ligand had been converted preliminarily into a substituted *N*-glucoside, and after that, the reaction gave complexes of the type **43** [with an amino group instead of the hydroxyl group at the C(1) atom of the sugar]. The ligand in this complex was either transformed into the aldehydo form of the type **39** or into the furanose (keto) form as a result of the Amadori rearrangement,[2] or remained in the native pyranose form.

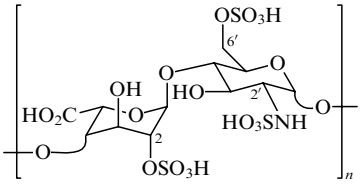
In order to model the chemical behaviour of natural polysaccharides containing residues of D-glucosamine **59a**, which might be able to form multi-ligand complexes, a ternary complex consisting of Cu^{II}, D-glucosamine, and prometon [2-methoxy-4,6-bis(isopropylamino)-*s*-triazine, PR] of the composition $[CuPR(LH_{-2})]$ was synthesised.[332]

The complex formation of other natural 2-amino sugars has been much less studied. It has only been reported that Cu^{II} forms complexes with D-mannosamine,[333] D-galactosamine, and D-talosamine.[334] The latter complex is the most stable among copper complexes of natural 2-amino sugars. This was explained [334] by the formation of a very strong hydrogen bond between the hydroxyl group at C(4) and the amino group at C(2), owing to their diaxial orientation.

An important constituent of natural glycolipids and glycoproteins is *N*-acetylneuraminic acid. The β-anomer of this acid **60a** forms [335–337] a fairly stable complex with Ca^{II} of the composition 1 : 1 (K_s = 121 litre mol^{-1}).[335] The calcium complex with *N*-glycolylneuraminic acid **60b** is even more stable (K_s = 193 litre mol^{-1}).[336]



60a–c



61

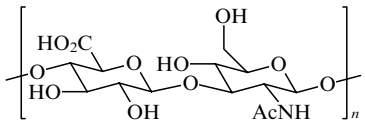
$R^1 = CO_2H$, R^2 = OH: R^3 = Me (**a**), CH_2OH (**b**);
R^1 = OH, $R^2 = CO_2H$, R^3 = Me (**c**).

The complex formation of Ca^{II} with the ligand **60a** has been reported [335] to involve the ring oxygen atom and the hydroxyl groups at the C(7), C(8), and C(9) atoms; however, according to another publication,[337] coordination occurs through the ring oxygen atom and the hydroxyl groups at C(2) and C(8). The natural α-anomer of the *N*-acetylneuraminic acid **60c** weakly binds Ca^{II};[337] binding of metal cations by the ligand **60c** becomes markedly stronger when Ca^{II} is replaced by Gd^{III} or Mn^{II},[338] which coordinate **60c** in the region of the glycerol 'tail' and the carboxyl group. Natural gangliosides (oligosaccharides containing the acid **60c** and long hydrocarbon chains attached to them [2]) coordinate metal cations by the glycerol fragment of the natural α-anomer **60c**. In this case, Ca^{II} ions are bound much more strongly than Mg^{II}.[339] However, since the *O*-methylglycoside of the α-anomer **60c** scarcely binds Ca^{II}, the coordination involves neighbouring monosaccharide fragments, in addition to the *N*-acetylneuraminic fragment.[340] A similar enhancement of complexation is also observed [341] in the binding of Gd^{III} by glycophorin A — a transmembrane glycoprotein with a high content of α-*N*-acetylneuraminic acid **60c**. In aqueous solutions, *N*-acetylneuraminic acids **60a**,**c** do not coordinate Na^+ and K^+ cations.[342]

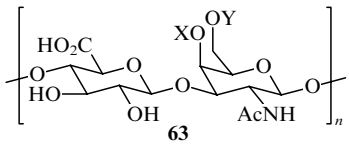
Glycosaminoglycans are polymers containing 2-amino sugars and occurring in connective tissues (mucopolysaccharides [2]); therefore, study of their complexation presents considerable interest from biochemical and medical viewpoints. A typical representative of mucopolysaccharides is an anticoagulant heparin.[343–345] The repeating disaccharide unit of this compound **61** consists (from left to right) of an L-iduronic acid residue sulfated at the hydroxyl group at C(2) and a D-glucosamine residue sufated at the amino group and at the hydroxyl group at C(6′). On dissolution in water, sodium heparinate dissociates only by 34%.[345] This corresponds to the normal behaviour of polyelectrolytes in which *s*-metal cations are bound non-specifically (territorial binding, Section II.1). In other words, they merely 'condense' on the negative charges in the polymeric chain,[346, 347] according to the Manning theory.[78] However, in another study,[348] specific binding of Na^+ by two carboxyl groups of the neighbouring L-iduronic acid residues was suggested, based on the results obtained by ^{23}Na NMR spectroscopy. However, later the same results were explained [349] in terms of the concept of condensation of counter-ions. On the other hand, in the case of Ca^{II}, ionic coordination with participation of the sulfo group of the L-iduronate and the sulfo group at the C(6′) atom of the D-glucosamine residue [351] has been suggested.[350] In the presence of excess Ca^{II}, neighbouring chains of the polymer are linked according to the 'egg box' pattern (Section II.1).[345] The complexation hypothesis is supported by the series of the efficiency of binding of *s*-metals with heparin [343, 352] ($Na^+ < K^+ < Mg^{2+} < Sr^{2+} < Ba^{2+} < Ca^{2+}$), since, according to the condensation theory,[78] the most efficient binding would be observed for the Mg^{2+} cation characterised by the maximum charge density. The data of circular dichroism spectroscopy,[353] which confirm this series, indicate simultaneously that there is no specificity in the binding of Ca^{II}. This contradiction might be explained by the fact that heparin is capable of both non-specific (condensation) and specific (complexation) binding of *s*-metal cations. This was discovered [354] for electrostatic binding of heparin with Zn^{II}. It has been noted [355] that this ability is peculiar only to heparin; however, according to another publication, heparin just possesses the highest affinity for Zn^{II} compared to other glycosaminoglycans.[356]

The interaction of heparin with Cu^{II} cations occurs as chelation involving the amidosulfate group.[357, 358] At higher pH, the complex formation is enhanced. This was explained [357–359] by straightening (despiralisaton) of heparin molecules resulting in liberation of new coordination sites. It was suggested [357] that Cu^{II} is coordinated inside the cavity of a helix, as in the case of Cu^{II} complexes with cyclodextrins (see Section III, the compound **51**). Among glycosaminoglycans, heparin possesses the highest affinity for $[Co(NH_3)_6]^{3+}$ cations, apparently due the high negative charge density in its macromolecule.[360]

Studies on the complexation of other glycosaminoglycans have also been concerned with hyaluronic acid (its dimeric unit **62** consists of the residues of D-glucuronic acid and *N*-acetylglucosamine **59b**) and chondroitinsulfates.[361] The latter compounds are built of dimeric units comprising a D-glucuronic acid residue and a residue of *N*-acetyl-D-galactosamine sulfated at the 4-position (chondroitin-4-sulfate, **63a**) or at the 6-position (chondroitin-6-sulfate, **63b**).



62



63

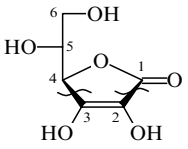
$X = SO_3^-$, Y = H (**a**); X = H, $Y = SO_3^-$ (**b**).

The presence of doubly charged *s*-metal cations ensures [362, 363] a helical conformation of hyaluronic acid **62**. In accordance with polarographic data, Cu^{II} forms complexes of the type CuL, CuL_2, and CuL_n (L is deprotonated hyaluronic acid).[364] In the former case (an inner-chain complex), Cu^{II} is chelated by the carboxyl group and by the bridging oxygen atom,[365] while at high pH values, the deprotonated *N*-acetyl group also participates in the coordination.[366]

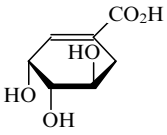
Chondroitin-6-sulfate **63b** binds Na^+ and Ca^{2+} ions non-specifically.[367] In terms of the strength of their binding to chondroitin-4-sulfate, *s*-metal cations can be arranged in the same sequence [361] as in the case of heparin (see above). In the case of chondroitin-6-sulfate, there is no difference between the strengths of binding of doubly charged *s*-metal cations.[361] For a mixture of chondroitinsulfates **62a**,**b**, it has been shown [368] that the efficiency of binding increases in the sequence $Cu^{II} < Yb^{III} < La^{III}$. In addition, chondroitin-4-sulfate **63a** binds Yb^{III} cations by the carboxyl group and the sulfo group of one chain and by two carboxyl groups of a parallel chain.[369]

V. Complexes of natural acids of the carbohydrate origin

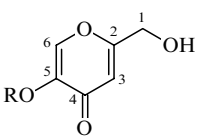
In this Section, we describe a number of complexones such as ascorbic (**64**), shikimic (**65**), kojic (**66**), and phytic (phytin, myo-inositol hexaphosphate, **67**) acids. These particular subjects were chosen due to their biosynthetic origin from carbohydrates.[2, 370, 371]



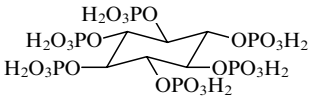
64



65



66a (R = H),
66b (R = CH_2COPh)

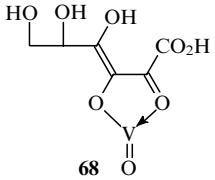


67

Numerous studies and a comprehensive review [9] covering publications up to 1977 have been devoted to metal complexes with ascorbic acid (vitamin C) **64**. Being a dibasic acid [owing to the protic activity of the hydroxyl groups at C(2) and C(3)], ascorbic acid **64** can be converted into two anions, $(LH_{-1})^-$ and $(LH_{-2})^{2-}$. It forms complexes $[M_xL_y]^z$, $[M_x(LH_{-1})_y]^z$, $[M_x(LH_{-2})_y]^z$, and $[M_x(LH_{-2})_yOH]^z$ virtually with all metal cations including oxo cations.[9] Salts of ascorbic acid **64** $[M_x(LH_{-1})]^z$ are formed upon coordination of a metal cation by the deprotonated hydroxyl group at C(3) (the strongest acidic site). The subsequent coordination involves the hydroxyl group at C(2) (either free or deprotonated) and the lactone carbonyl group at C(1). The vicinal hydroxyl groups in the 'tail' at the C(5) and C(6) atoms do not participate in the coordination in solutions,[372, 373] although in the condensed phase, this coordination is possible.[374–377] Thus in solid Tl^I ascorbate, the metal ion is additionally bound not only to the hydroxyl groups at C(5) and C(6) but also to the lactone carbonyl group. In solid ascorbates of divalent *s*-metals, a cation is coordinated to three anions, and only Mg^{II} binds two anions.[379] In aqueous solutions, cations of univalent *s*-metals are bound by an ionic bond, except for Li^+, which is bound by a covalent bond.[380]

In the case of In^{III} and Ga^{III}, polynuclear complexes predominate in acidic media,[381] while lanthanides form [381] complexes $[M(LH_{-1})_2]^+$. The following stability series has been elucidated [382] for the complexes of divalent metals: Be > Pb > Mn > Fe > Co > Ni. These metals form complexes of the composition 1 : 1, and only Be^{II} forms stable 1 : 2 complexes.[382]

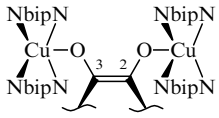
Complex formation of V^{IV} [9, 380, 383] and V^V,[384] which is accompanied by oxidation of the ligand yielding dehydroascorbic acid, has been studied in detail. Upon the reaction with V^{IV}, dehydroascorbic acid undergoes the lactone ring opening being thus converted into diketogulonic acid. Chelate **68** is formed apparently from the enol form of this acid and the vanadyl ion.[372, 373, 385–388]



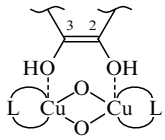
68

Complex formation of ascorbic acid with *d*- and *f*-metal cations has been studied.[9] This ligand forms solid three-dimensional polymeric complexes with Zn^{II}, Co^{II}, and Hg^{II}.[389] In solutions, monodentate [through the O(3) atom] or bidentate [through the O(2) and O(3) atoms] coordination is possible.[389] The complexes of the acid **64** with Co^{II} in solutions have been studied in most detail.[9] A study of spin–lattice relaxation in the ^{13}C NMR spectra has confirmed [390] the predominant chelation of Co^{II}, Fe^{II}, and Mn^{II} by the O(2) and O(3) atoms, while the lactone and ring oxygen atoms and the hydroxyl groups at C(5) and C(6) are weaker coordination sites.

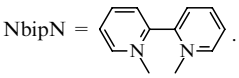
The reaction of the acid **64** with $[Co(NH_3)_4]^{2+}$ gives two complexes: a monodentate complex [with coordination through O(3)] and a bidentate one (with coordination to the lactone and ring oxygen atoms).[391] A stable ternary complex **69** formed by ascorbic acid and bis(2,2′-bipyridyl)copper(II) has been described.[392] Binuclear complexes of Cu^{II} **70** are readily reduced by ascorbic acid **64** if the sizes of the reactants are fitted in the intermediate complex **70**.[393]



69

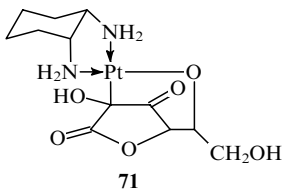


70



An unusual organometallic complex of platinum with ascorbic acid (**71**) containing a C–Pt σ-bond has been synthesised within the framework of studies dealing with the development of new anticancer preparations.[394] Complexes of the acid **64** with dicyclopentadienyltitanium $[\eta\text{-}C_5H_5)_2TiL_2]$ and with dialkyltin $[R_2SnL \cdot H_2O]$ (R = Me, Et) have also been obtained.[395] In the latter complex, the ligand L can be coordinated both in monodentate [by O(3)] and bidentate [by O(2) and O(3)] fashions.

Shikimic acid **65** forms [396] a (1,2-diaminocyclohexane)platinum complex similar to the compound **71** prepared from ascorbic acid [the metal is coordinated to the carboxyl oxygen atom and to the alkene carbon atom C(2)].



71

Kojic acid **66a** containing an oxo-enol fragment forms numerous complexes with various cations [371, 397] including *s*-metal ions.[13, 371] The compounds of kojic acid with metal ions can be built [371] either as complex salts with coordination to the oxygen atom at C(6) or as chelates with an additional coordination to the oxo group. Synthetic 5-phenacylkojic acid **66b** also acts as a complexone.[11, 398–400] In its complexes, a metal ion is linked to

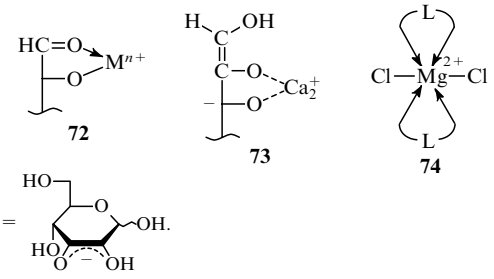
the carbonyl fragment of the phenacyl group, to the carbonyl group at C(4), and to the oxygen atom at C(6).

The formation of metal complexes with phytin has been intensely studied due to the dietary significance of this compound (Section VI.1). The thermodynamics of phytin complexation with Ca^{II},[401] Zn^{II},[402] Cu^{II},[403] Mn^{II},[404] Co^{II}, Ni^{II},[405] Fe^{III}, and Cr^{III} [406] have been studied by calorimetry. Complex formation of incompletely substituted ester, myo-inositol 1,2,6-triphosphate, with alkali[407] and transition[408] metal cations has been investigated. For none of the complexes obtained, has the structure been determined.

VI. The significance and applications of metal coordination to carbohydrates

1. The influence of complex formation on the chemical properties of carbohydrates

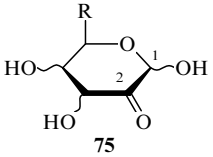
The catalytic role of metal cations in a key transformation of carbohydrates, namely, in the Lobry de Bruyn – Alberda van Ekenstein rearrangement[2,409] [epimerisation of aldoses at the C(2) atom and their conversion into ketoses], has been explained by assuming the intermediate formation of complex **72**.[409] In a discussion of the dehydration of carbohydrates, the special case of alkaline dehydration of D-mannose was interpreted using the suggestion[410] of formation of a enediol complex of type **73**. The formation of similar enediol metal complexes has been assumed[411] to rationalise the mechanism of oxidation of monosaccharides by hydrogen peroxide. These complexes have been identified by electronic and NMR spectroscopy.[412] The enediol complex **74** has been isolated and characterised.[413]



Thus, the hypothesis of the formation of enediol forms of carbohydrates stable as metal complexes, put forward[2,370] to account for the above transformations, can be considered to be experimentally proven. However, in view of the most recent results, participation of these species in epimerisation seems doubtful (see below).

Angyal *et al.*[6,414–417] have shown that *O*-glycosylation according to Fischer (treatment of sugars with a methanolic solution of HCl)[2] carried out in the presence of calcium or strontium salts results in increased yields of *O*-methylfuranosides. This discovery made this type of compound readily accessible. Acyclic forms, aldose dimethyl acetals, can also be formed under these conditions.[418]

The promotory effects of Ca^{2+} and Ba^{2+} ions on the alkaline oxidation of aldoses by 2-anthraquinonesulfate to aldonic acids of the type **14a** has been explained[419] by the fact that the stability of the intermediate aldos-2-uloses **75** increases when these metal ions are coordinated to the hydroxyl group at the C(3) atom and to the oxo group. The angle between the two coordinate bonds must be 0 – 30 °; otherwise, the influence of these cations is not manifested.



75

R = H, CH_2OH.

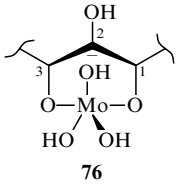
Complexation with boric and phenylboronic acid has been used[420] to perform selective acetonation of monosaccharides; a similar approach used in the series of nucleosides and nucleotides is employed for their selective methylation at the base.[421] The use of a complexing polymer, polystyrylboronate, made it possible to prepare partially acetylated derivatives of *O*-methylglycosides, valuable from the synthetic viewpoint.[422] The addition of a borate during the aldol condensation of 2-acetamido-2-deoxy-D-glucose **59b** with oxaloacetate giving *N*-acetylneuraminic acid (a mixture of anomers **60a**,**b**) increases the yield of the product. Apparently, complexation suppresses side reactions.[423] The presence of a borate shifts the aldose ⇄ ketose equilibrium (the Lobry de Bruyn – Alberda van Ekenstein rearrangement[2,409]) towards the latter.[424,425] Cations of *d*-metals also catalyse this rearrangement.[426] It was shown[427,428] that the main event in the catalytic action of sodium aluminate on the isomerisation of D-glucose to D-fructose is stabilisation of the intermediate enediol *via* coordination giving a structure like **73**. The presence of an anion exchanger in the paramolybdate form also facilitates this transformation by suppressing side reactions.[429]

Complex formation has been successfully used to protect particular functional groups during selective *N*-acylation of aminoglycoside and aminocyclitol antibiotics in the presence of heavy metal salts.[430–432] The direction of acetylation can be changed simply by changing the metal cation used.[430]

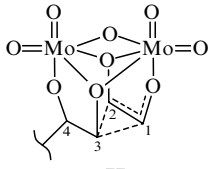
The numerous reactions of oxidation of aldoses in the presence of metal salts often yield initially intermediate metal complexes the stability of which varies over wide limits. Complex formation can occur in a transition state, or it can give highly unstable complexes.[433,434] The intermediates can decompose either in a single-electron process giving free radicals, which act as the reactive species,[435–438] or by a two-electron transfer mechanism giving reaction products.[439–441]

In a number of studies,[442–458] a preparative method has been developed, based on the ability of molybdate ions MoO_4^{2-} to catalyse epimerisation of aldoses and ketoses and their derivatives in relation to the carbon atom nearest to the carbonyl group. The most prominent example of this epimerisation,[202] the transformation of D-xylofuranose into D-lyxose, was discussed in Section II.3. When molybdate is replaced by tungstate, the complexation is not accompanied by epimerisation,[459] because the carbohydrate complexes of tungstate are much more stable than the molybdate complexes[198] (see Section II.3). However, in the presence of a borate, D-arabinose incorporated in the tungstate complex readily epimerises to D-ribose, since the borate complex of the latter is more stable.[460]

Previously, the mechanism of epimerisation has been interpreted by assuming[13,442] the intermediate formation of planar complex **76**, deprotonated at the C(2) atom, in which the metal is coordinated to the O(1) and O(3) atoms of the cyclic form of the substrate. The subsequent diastereofacial protonation of the complex **76** was assumed to give both the complex of the substrate and that of the product. However, later, using NMR spectroscopy of aldoses enriched in the ^{13}C and ^{2}H isotopes at the C(1) atom, it was shown[461] that in reality, this epimerisation includes a rearrangement of the substrate carbon skeleton. The C(1) and C(2) atoms exchange their positions in the hypothetical binuclear transition complex **77** containing the initial aldose in the acyclic aldehydo form. A similar complexation has been proposed[462] to explain epimerisation of D-glucose to D-mannose catalysed by $Mo_7O_{24}^{2-}$ ions.

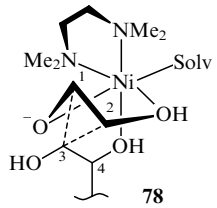


76



77

It has been suggested [13,463,464] that in the presence of Ni^{II} and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, aldoses are wholly epimerised at the C(2) atom with a similar rearrangement of the carbon skeleton *via* transition complex **78** with the aldehydo form of the substrate. An analogous reaction occurs when Ca^{II} is used instead of Ni^{II}.[465] Finally, it has been found [466] that a rearrangement of the carbon skeleton of carbohydrates accompanied by epimerisation occurs even in such a simple system as methanol–calcium hydroxide. It is obvious that in view of these findings, the generally accepted mechanisms of the Lobry de Bruyn–Alberda van Ekenstein rearrangement [409] should be revised. In the methanol–Ni^{II}–*N*,*N*′-diethylethylenediamine system, D-fructose **29** undergoes a more extensive rearrangement of the carbon skeleton resulting in a branched aldose, 2-C-hydroxymethyl-D-ribose.[467] It is noteworthy that the side formation of ketoses in these processes is not accompanied by a rearrangement of the carbon skeleton of the initial aldoses.[466] Apparently, ketoses are formed *via* the generally accepted mechanism of the Lobry de Bruyn–Alberda van Ekenstein rearrangement.[2,409] The discovery of the change of the carbohydrate carbon skeleton upon the formation of metal complexes is undoubtedly an outstanding achievement in the coordination chemistry of carbohydrates.



78

Solv is solvent.

2. Reactions involving metal complexes of carbohydrates

Cyclodextrins react with $RhCl_3$ to give colloidal dispersions of rhodium, which efficiently catalyse hydrogenation of alkenes carried out at 30 °C under atmospheric pressure of hydrogen.[468] Complexes of Cu^{II} with β-CD and its polyphosphate initiate vinylic polymerisation.[469] Sugars are often used as donors of hydrogen in the catalytic hydrogenation of carbonyl compounds with hydrogen transfer.[470] The mechanism proposed for this process [470] assumes participation of metal complexes of carbohydrates formed intermediately. One example of the use of cyclodextrin as phase transfer catalyst, owing to its ability to coordinate *s*-metal cations, was reported.[471]

The chirality of carbohydrates is employed in enantioselective catalysis. Well known [472–475] catalysts for hydrogenation are L-tartaric acid **18** or its D-enantiomer adsorbed on the metal surface; in this case, chelation leading to the formation of a chiral environment on the metal surface is assumed. The optical yields in these reactions reach 55%–63%.[476–478] This is a significant achievement, because these catalysts can be used repeatedly. Similar reactions catalysed by palladium supported on cellulose [479] resulted in optical yields of only 0.10%–0.15%. Apparently, in the latter case, no metal binding on the surface of a chiral support is involved. The optical yields in the reduction of the complexes of ferrocenyl ketones with β-CD of the type **52b** vary from 5% [480] to 32%–80%.[481,482]

3. Modelling of enzymes by metal complexes of carbohydrates

This field of application of carbohydrate metal complexes is still limited to cyclodextrins. Thus alkaline hydrolysis of *p*-nitrophenyl acetate is suppressed almost entirely by the addition of the binuclear complex of Cu^{II} with α-CD **51**.[483] When the corresponding complex with β-CD is used, the retardation of the reaction is less pronounced. This is due to the formation of a stable inclusion compound from the former complex and the substrate; this permits regarding this complex as an adequate model of a metal enzyme.[483] A structurally related binuclear complex of Mn^{II} with β-CD has been proposed [484] as a model of a photosynthesis enzyme, which catalyses water oxidation to oxygen. It has been shown [485,486] that complex formation of *d*-metals with cyclodextrins is a general way of stabilising hydroxo complexes of *d*-metals for the modelling of terminal enzyme systems for photosynthesis.

One aspect of enzyme activity, namely, the decrease in the number of degrees of freedom of the substrate upon its complexation with the enzyme, has been modelled by alkaline hydrolysis of esters of ferrocenecarboxylic acids.[487–490] The molecular design was accomplished in such a way that the catalytic centre (a hydroxyl group of cyclodextrin) was located in the optimum vicinity of the reaction centre of the substrate when the latter had entered the cyclodextrin cavity.[487–490]

4. Analytical methods based on the formation of metal complexes with carbohydrates

An important application of complex formation with metals is the solution of analytical and structural problems in the series of carbohydrates.

A large set of qualitative and quantitative electro(iono)phoretic and chromatographic methods for the separation of sugar mixtures based on the complexation with metals have been developed. Early [491,492] and more recent [493] reviews survey the data on paper electrophoresis of sugar mixtures in aqueous solutions in the presence of various salts such as borates, germanates, stannates, arsenites, molybdates, and tungstates. It is significant that these modifications of the method supplement one another. Other efficient procedures are paper electrophoresis in the presence of Cu^{II} periodate, tellurate,[494] acetate, and basic acetate [150,495] and capillary electrophoretic separation of enantiomeric monosaccharides in the borate–dextrin (cyclodextrin) system, *i.e.* under conditions of double complexation.[496] Electrodialysis through a polymeric membrane with grafted boric acid residues has been proposed as a method for separation of multicomponent product mixtures obtained upon the formose reaction.[497]

A broad range of methods consisting in paper and column chromatography of carbohydrates based on complex formation with metals have been surveyed in a review.[493] The main column chromatography technique is ion exchange chromatography using Li^+, K^+, Ca^{2+}, and Ba^{2+} forms of cation exchangers and cellulose or silica gel impregnated with a borate. Column chromatography of aqueous solutions of sugars on alumina is also accompanied by complex formation.[498] Closely related approaches are chromatography on anion exchangers in the aluminate form [499] and chromatography on paper (cellulose) containing carboxylate groups grafted as La^{3+}, Ca^{2+}, and Ba^{2+} salts.[500] Yet another efficient method is thin layer chromatography of sugars and their derivatives using the Ca^{2+} and La^{3+} forms of cation exchangers.[501] Racemic mixtures of ferrocene derivatives are readily separated on polyamide when an aqueous solution of β-CD is used as the eluent.[502]

Complex formation with metals has long been used for the determination of sugars. The most widely used procedures are the quantitative Bertrand method [503] based on oxidation of copper complexes of aldoses to give Cu^{I} oxide and the related qualitative Fehling [2] and quantitative Somogyi [504] methods. There are grounds for believing that oxidation occurs in enediol Cu^{II} complexes.[505] Determination of sugars based on their oxidation by the Cu^{II} periodate complex [506] or Ce^{IV} sulfate [507] has also been described.

The formation of complexes of carbohydrates with metals proved to be useful for electrochemical, mainly polarographic, determination of metals. In the presence of acyclic or cyclic polyols, the half-wave potential of the metal cation being analysed substantially shifts, which enables its determination in the presence of other metal cations.[508–510] The volumetric determination of Pt^{II} in an alkaline solution of D-mannitol in the presence of

cations of other platinum metals is another example of this approach.[511]

It is difficult to overestimate the role of complex formation in the configurational and conformational analysis of carbohydrates.[512, 513] Thus, determination of the stability constants of the borate complexes of pyranoses permitted Angyal to propose a method for the calculation of the conformation energies of these ligands,[512, 513] while the change of the specific rotation of aldoses following their complexation with borate made it possible to determine their anomeric configuration.[2, 3]

Several methods of the conformational analysis of carbohydrates are based on the correlation between the complexing and rotational (chiroptical) properties of ligands [optical rotatory dispersion (ORD) and circular dichroism (CD) spectroscopy [514–518]]. Thus CD spectroscopy of molybdate complexes has revealed [469] a correlation between the orientation of the hydroxyl groups at the C(2) and C(3) atoms in the pyranose form (see the structures **4a**,**b**) and the signs of the Cotton effects in the CD spectrum of a colourless solution of the molybdate complex. Chiroptical methods are applied most often to solutions of coloured metal complexes containing Cotton-genic (manifested in the visible ORD and CD spectra) groups. This line of research was initiated by the classical studies of Reeves [4] dealing with the rotational properties of copper complexes of *O*-methylglycopyranosides. As a result of these studies, a clear correlation between the sign of rotation of model compounds with a fixed arrangement of the hydroxyl groups and the sign of the dihedral angle between them was elucidated. Later, these results were confirmed by chiroptical methods [135, 519–522] (ORD and CD spectroscopy). Similar correlations have been found for Ni^{II} complexes of carbohydrates.[227, 228, 523, 524] Other Cotton-genic derivatives such as Mo^{II} acetate [525] and other *d*-metal acetates,[526] which form chiral complexes with vicinal diol groups of sugars, proved to be more convenient compounds from the viewpoint of methodology.

Complex formation of sugars with lanthanide cations used as shift reagents has also found a wide utility in the conformational analysis of carbohydrates by NMR spectroscopy.[243–245, 527–537] Boric acid [538] and Cu^{II} cations [139, 539] have also been used as shift reagents.

The complex formation of sugars with metals has been employed [540–542] for improvement of the mass spectrometry methods for their identification. The complexation of anthrylboronic acid with sugars is accompanied by quenching of its fluorescence; therefore, it has been used [543] for the development of fluorescence chemical sensors for sugars.

5. The significance for biology and medicine

Previously the views on the biological functions of carbohydrates reduced to their food (glucose, fructose, starch) and structural (cellulose, chitin) properties. However, during the last decades, carbohydrates have been found to play a crucial role in a number of vitally important processes such as mutual recognition of molecules and cells (cell adhesion, agglutination, reception),[544] tissue calcification as the initial stage of the formation of vertebrate bones and shells of molluscs and bird eggs.[545] These discoveries substantially raised the biological status of carbohydrates. Since all the processes listed above are Ca^{2+}-dependent, this has also stimulated studies dealing with the complex formation of carbohydrates with *s*-metal cations (Section II.1). The studies performed have demonstrated that carbohydrates are weak complexones for these cations and that complex formation with *s*-metals cannot play an important role in the above biological processes. For example, *N*-acetylneuraminic acid **60c**, which is an indispensable component of biologically significant oligo- and polysaccharides, forms Mg^{II} and Ca^{II} complexes in aqueous solutions the stability constants of which are 1.5 and 1.9 litre mol^{-1}, respectively.[342] Since in a living organism, carbohydrates are almost necessarily linked to proteins (glycoproteins and proteoglycans [2]), a number of studies [546–548] have been devoted to the complex formation of a model cation (Gd^{3+}) with synthetic glycopeptides. It was found that coordination occurs both in the carbohydrate and peptide fragments, the latter being preferred. In general, there are no grounds to believe that complexation of carbohydrates themselves plays a significant role in biological processes. The examples given below confirm this point.

When sugars are specifically bound by protein compounds, lectins,[549–552] in the presence of metal cations, the protein–sugar interaction is accomplished only by hydrogen bonds.[552] Apparently, metal cations ensure the appropriate conformation of the protein needed for sugar reception.[549] At a certain stage of cell recognition, interaction of carbohydrate-containing proteins is due to the Ca^{2+} cation, but it is unknown to what particular fragment this ion is coordinated. By analogy with lectins, it can be assumed that in this case, too, the metal ion is coordinated to the protein fragment.[553, 554] The complex formation of Ca^{2+} with sulfated polysaccharides is considered to play a certain role in its deposition in tissues.[545]

Metal complex formation with natural carboxylic acids of carbohydrate origin (see Section V) is important for medicine. Thus ascorbic acid decreases the level of mutations in workers in contact with heavy metals.[555] Phytic acid is present in substantial amounts in vegetable oils, and its ability to form an insoluble complex with Ca^{2+} decreases the removal of calcium with urine.[556] Binding with heavy metal cations can even inactivate metal-dependent enzymes, for example, α-amylase [557] and carboxypeptidase A.[558]

The platinum complexes **46** [236] and [PtL(1,3-diamine)] [242] (L is D-gluconate or D-glucuronate) exhibited a considerable antitumour activity. This activity was also found for the platinum complex **71**.[394] Polymeric osmium carbohydrate complexes, osmarines,[238, 239] (Section II.3) are used as antiarthritis preparations owing to their capability of binding superoxide ions, which are responsible for this disease.[239] Copper(II) complexes with cyclodextrin of the type **51** can be used [559] for treating the mildew blight of grapes, because these compounds are not toxic in wine. Water-soluble iron complexes of glucose and fructose **42** are used to treat anemia.[560] Phytin **67** prevents foodstuffs from going bad under the action of atmospheric oxygen, because it binds Fe^{3+} and Cu^{2+} cations, which can act as efficient catalysts for undesirable oxidation processes.[561]

The complex formation of metals with polysaccharides has also found use in medicine. Pectins (polymers of the type **5** with partly esterified carboxyl groups) isolated from fruits or vegetables efficiently bind toxic metal cations and thus they can be used for detoxification of an organism.[562] It has been proposed [563] to use iron complexes of chondroitinsulfates **63a**,**b** for curing iron deficiency anemia. Metal complexes of dextran and inulin can be used as paramagnetic contrasting reagents [564] in medical NMR spectroscopy. Treatment of cellulose with heavy metal salts and subsequent interaction with antibiotics imparts antibacterial properties to textiles.[565]

In nature, complex formation of metals with polysaccharides can be undesirable. Thus the formation of gels on the surface of plant roots may have negative consequences for plants, since their main components, acidic polysaccharides, bind metal cations, which come directly from soil particles and are needed for nutrition.[566]

s-Metal cations [567] and *d*-metal cations [568] are used to strengthen agaroid jellies. *d*-Metal hydroxides treated with sugars are employed for enzyme immobilisation.[569] The natural polymer of *N*-acetyl-D-glucosamine — chitin — has been proposed [570] as a reagent for extraction of heavy metals from waste water; the ferrite–alginate system is employed for the preparation of ferromagnetic particles used as a contrasting reagent [571] in NMR spectroscopy for medical purposes.

VII. Conclusion

The modern coordination chemistry of carbohydrates resembles an enormous picture painted with rough strokes in which only some sections are drawn thoroughly. This is due to the extreme complexity of the investigation subjects, caused by the specific character of carbohydrates as complexones. Carbohydrates can exist in both cyclic and acyclic forms; they can act as polydentate ligands and form regioisomeric complexes. In addition, chirality of carbohydrates results in the formation of unequal amounts of diastereoisomers in relation to the chelate unit. This diversity of compounds can be found in a single reaction mixture. Therefore, the overwhelming majority of conclusions concerning the structures of carbohydrate metal complexes have been drawn relying on more or less likely suggestions, except for those few cases where researchers were able to obtain a crystalline compound and study its structure by X-ray diffraction analysis. However, with the advent of NMR techniques using metal cations as shift reagents, it became possible to determine fairly reliably the structures of a number of metal complexes of carbohydrates in solution. It would hardly be an overstatement to say that nowadays the coordination chemistry of carbohydrates experiences a new stage of its development.

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